Land use interactions drive southwestern Ontario stream nutrient concentrations

Renee L. Lazor
The University of Western Ontario

Supervisor
Adam Yates
The University of Western Ontario

Graduate Program in Geography
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science

Land use interactions drive southwestern Ontario stream nutrient concentrations

(Thesis format: Monograph)

by

Renee Lazor

Graduate Program in Geography

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

Abstract

Human activities have transformed the landscape and altered natural habitats through intensive land uses including agriculture and urbanization. Identifying land use drivers of tributary nutrient concentrations and describing the strength and direction of this relationship is critical to improve management of water quality in basins draining into the Great Lakes. The overarching goal of my thesis was to quantify the cumulative influence of spatial patterns in land use and land cover on variation of nutrient concentrations in tributaries of the Great Lakes. Biweekly water chemistry samples were collected from 29 streams located in southern Ontario between May and November, 2012. Agriculture, urbanization and the population served by a municipal sewage treatment plants (STPs) were quantified for each stream at multiple spatial scales. Ordinary least squares regression analysis identified relationships between nutrient parameters (NH_3, TKN, NO_{3-}+NO_{2-}, TN, SRP, and TP; but not TDP) and land use descriptors. Concentrations of NO_{3-}+NO_{2-} was driven by a combination of urban and agriculture land use in the catchment whereas concentrations of NH_3, TKN, and SRP were related to agriculture and STPs. TN and TP were only associated with STP population served per km^2. Model predictive performance was evaluated under three scenarios: data comparability, spatial robustness and temporal robustness (dry, moderate and wet climate scenarios). Overall, assessment of model performance indicated that data sampling and collection protocol may limit prediction accuracy. Results show that human activities are significant drivers of stream nutrient concentrations and that nitrogen forms can be predicted, on average, in 70% of evaluation streams under most scenarios. Findings demonstrate the utility of land use as a predictive tool for managing stream nutrient concentrations. The nitrogen models generated in this study could be used to enable planners and managers to better understand the potential implications of future land management decisions on water quality.

Keywords

agriculture, Great Lakes Basin, land use, model evaluation, municipal waste water treatment plants, river systems, southern Ontario, stream nutrient variability, tributary streams, urbanization, waste water effluent, water chemistry

Acknowledgments

First I would like to extend an enormous amount of gratitude to Adam Yates, the humble leader of our lab and fearless captain. Throughout my project Adam has been available to discuss and problem solve the little and big issues, providing guidance and words of encouragement, and I am so grateful to have him as a supervisor. His dedication to family and research has been both an inspiration and motivation throughout the journey.

I also must thank Patricia Chambers and the team from Environment Canada for the opportunity to be a part of the Great Lakes Nutrient Initiative. You provided me with a team of scientific leaders to learn from and have engaged me in research directed towards one of the greatest freshwater ecosystems on the planet, for that I am eternally grateful. Also, thank you to my committee members, Patricia Chambers and Irena Creed, for their input and guidance through the project.

A special thanks to all those people who were engaged in and responsible for the organization and collection of data including the countless hours spent collecting samples, installing equipment and splashing around in the streams of southwestern Ontario. Cheers to; Zoey Duggan for teaching me the technical aspect of field work and for being a great leader; Erika Hill for friend, field and lab support; Daryl Halliwell for being a magician in the stream; and a big thank you to the multitude of people who donated many of their days and hours to fun field times (Pablo Banuelos, Co-op Chris, Shirley Ngai and the plethora of techs from CCIW). A big high five and hug also goes out to my lab mates; Edward Krynak, Roger Holmes, Chris Chesworth and Natalie Izral. You have filled the days with laughter and support while helping answer the big questions during those times when it feels like things are unravelling.

Finally, a special thank you to my family and friends who have been incredibly supportive throughout my quest to study 'the nature'. Mom and dad you have taught me the importance of kindness and hard work, thank you for your love and support (even when I am a grumpy bear). My sister, Shell, thank you for being my best friend and keeping me in check; to Jay, for challenging me to make the dream come true; and to the little people, Autumn and Connor, who discover something new every time we are in ‘the nature’, thank you for your hugs and wisdom. With sincerity I hope that the knowledge gained from the past two and a half years of study will encourage people to be stewards of a better earth, from the land to the sea.

Table of Contents

List of Tables

List of Figures

List of Equations

List of Abbreviations

AAFC – Agriculture and Agri-food Canada

AVHRR – Advanced Very High Resolution Radiometer

BMP – Best Management Practice

Buf – 30m stream buffer

C – Catchment

CA – Conservation Authorities

CCME – Canadian Council of Ministers of the Environment

CV – coefficient of variation

CWQO – Canadian Water Quality Objectives

Ef – Nash Sutcliffe Efficiency Index

DEM – Digital Elevation Model

ESRI – Environmental Systems Resource Institute

GIS – Geographic Information System

GLNI – Great Lakes Nutrient Initiative

GLWQA – Great Lakes Water Quality Agreement

GME – Geospatial Modelling Environment

HW – head waters

MAD – Mean Absolute Deviation

MAE – Mean Absolute Error

MSE – Mean Square Error

NDVI – Normalized Difference in Vegetation Index

NH_3 – ammonia (total)

NLET – National Laboratory for Environmental Testing

NO_3- + NO_2- – nitrate and nitrite

O:E – Observed:Expected

Ō:Ē – Average of the observed:average of the expected

OLS – Ordinary Least Squares Regression

OMOE – Ontario Ministry of the Environment

PWQMN – Provincial Water Quality Monitoring Network

PWQO – Provincial Water Quality Objectives

RIVPACS – River Invertebrate Prediction and Classification System

RMSE – Root Mean Square Error

SD – Standard Deviation

SRP – soluble reactive phosphorus

STP – Sewage Treatment Plant

SWO – southwestern Ontario

TP – total phosphorus

TDP – total dissolved phosphorus

TKN – total Kjeldahl nitrogen

TN – nitrogen

USGS – Unites States Geological Survey

VIF – variance inflation factor

600m – 30m stream buffer 600m upstream from the site

1 Introduction

1.1 Cultural Eutrophication

Eutrophication is defined as the increase in primary productivity as a result of the addition of nutrients, primarily phosphorus and nitrogen, to aquatic systems (USGS, 2013). In the Great Lakes basin, eutrophication has resulted in anoxic conditions in parts of Lake Erie and certain embayment's of Lake Huron, and degraded water quality affecting drinking water, recreation, biological processes and ecosystem function. In the 1970's the government of the United States of America and Canada established the International Joint Commission to manage trans-boundary water issues and issued the Great Lakes Water Quality Agreement (GLWQA 1972). Municipal waste water and changed land use were identified as being the primary sources of nutrients that were responsible for eutrophication of Lake Erie. Increases in nutrient concentrations have been attributed to human activities, with geology, soil and vegetation also influencing the concentration of nutrients transported into aquatic ecosystems (Alexander et al., 2008; Baker et al., 1985; Barton et al., 1997; Houser et al., 2010; Johnson et al., 1997; Sliva et al., 2001; Yates et al., 2006). Excess input of nutrients enhance the process of eutrophication and has resulted in fundamental changes to the ecological function of waterways, impairing the ecological health of aquatic ecosystems within the region (Ontario Ministry of Environment and Energy. 1994; Carpenter et al., 1998; Dodds and Oakes, 2008; Houser et al., 2010; Chambers et al., 2012; Klose et al., 2012). To mitigate this nutrient influx, waste water treatment facilities were upgraded and land management practices were initiated (Environment Canada, 2012). However, reoccurrence of blooms within Lake Erie in the 1990's through the present has renewed interest in identifying factors contributing to nutrient influx to tributaries of the Great Lakes.

In support of the GLWQA (amended 2012) the Great Lakes Nutrient Initiative (2012) was put into action by Environment Canada. This initiative identifies five priority activities:

1) Establishing current nutrient loadings from selected tributaries;
2) **Enhancing knowledge of the factors that impact tributary and near shore water quality, ecosystem health, and algal growth;**

3) Establishing bi-national lake ecosystem objectives, phosphorus objectives, and phosphorus load reduction targets;
4) Developing policy options and strategies to meet phosphorus reduction targets;
5) Developing a bi-national near-shore assessment and management framework.

(Adapted from: Government of Canada, Environment Canada, 2012)

This project focuses on priority 2, identifying human activities that impact tributary water quality for Lake Erie. Specifically, this project aims to describe the temporal variation of nutrient concentrations throughout the growing season of 2012. The project attempts to identify 'critical periods' throughout the growing season that are characterized by changes in vegetation condition. Vegetation condition refers to the photosynthetic activity and canopy structure which vary through the dormant, emergent, active, and senescent phases through the lifecycle of vegetation. For each 'critical period' the drivers of seasonal changes in nutrient concentrations may be identified and the relative influence of important human activities (agriculture, urbanization and waste water treatment) on nutrient concentrations will be quantified for tributaries of Lake Huron and Lake Erie. This project develops parsimonious models that identify significant drivers of tributary stream nutrient concentrations using multiple spatial scales of agriculture, urban and sewage treatment plant (STP) descriptors. The performance of the derived nutrient models is evaluated under five scenarios. Performance measures assess the utility of the derived models as a predictive tool for the management of water quality in tributaries of Lake Erie and Huron.

1.2 Land use and Water quality

The physical and chemical conditions of river systems are a function of catchment characteristics and influenced by the geology, climate and land cover in a region (Hynes, 1975; Vannote et al., 1980). In river systems the biogeochemical cycle is driven by precipitation that mobilizes inorganic and organic matter from the landscape for transport to the streams and rivers (Vannote et al., 1980). Human activity has altered the availability and loss of nutrients and sediment from the catchment resulting in dramatic changes in the physical and chemical condition of streams and rivers (see review by Allan 2004; Carpenter et al., 1998). Multiple studies have shown an association between the degradation of stream water quality with the expansion of human activity in the catchment, including the increasing footprint of agriculture and urban development (Carpenter et al., 1998; Chambers et al., 2008b; Dodds et al., 2008; Johnson et al., 1997; Omernik, 1977; Paul & Meyer, 2001). The increased availability of nutrients has enhanced eutrophication of water bodies. Determining the influence of land use practices on stream nutrient concentrations is, therefore, important for the management of water quality and mitigation of eutrophic and hyper-eutrophic waters.

Stream, river and lake nutrient concentrations are influenced at a landscape scale by non-point sources and point sources of pollutants originating from human activities. Non-point sources of pollutants include agriculture and urbanization, which contribute nutrients to surface waters through surface and subsurface runoff following precipitation events (Carpenter et al., 1998; Paul & Meyer, 2001). In agriculturally dominated regions, common land management practices, including the application of fertilizers and manure, can introduce excess nutrients to the ecosystem as non-point source pollution (Allen, 2004; Baker et al., 2003; Dodds et al., 2012; Houser et al., 2010, Klose et al., 2012; Sanchez-Perez et al., 2009; Withers et al., 2003). Row cropping and tile drainage alter the interaction of precipitation with the landscape resulting in increased runoff that enhances the delivery of nutrients to the river network (Baker, 2003; Carpenter et al., 1998; Dolan et al., 2012; Johnson et al., 1997). The cumulative effects of these land management practices may include excessive growth of algae and macrophytes that can alter the gross primary productivity of streams (Hudon & Carignan, 2008; Sanchez-Perez et al., 2009). In some cases the outcome of these practices are catastrophic, resulting in de-oxygenated zones and algal blooms in downstream ecosystems, such as those identified in the Gulf of Mexico and Great Lakes (Houser et al., 2010; Michalik et al, 2011).

In urban-dominated regions, fertilizers, detergents and solvents are sources of nutrients that can be entrained in surface runoff during precipitation events (Carpenter et al., 1998; Paul & Meyer, 2001). In areas where native vegetation has been removed from the landscape, such as with construction of semi-impervious surfaces in urban areas (parks, lawns, golf courses) and commercial agriculture, nutrients are topically applied and rapidly transported to nearby streams through precipitation, infiltration and runoff events (Allen, 2004; Carpenter et al., 1998; Paul & Meyer, 2001). This rapid influx of surface and subsurface water potentially introduces sediment and nutrients thus influencing stream water quality (Allen, 2004; Carpenter et al., 1998). Land management practices aim to minimize nutrient losses from land to water by trapping sediments and solutes (Johnson et al., 1997; Lu et al., 2009; Morse et al., 2014). It is therefore important to recognize that the influence of non-point sources varies spatially throughout the watershed due to variation in land use and management practices and temporally as a result of differences in annual, seasonal and event scale changes in meteorological conditions and the interaction with land use/land cover.

In urban areas, wastewater treatment facilities, such as sewage treatment plants (STPs) and sewage lagoons, can act as point sources of nutrients (Chambers et al., 1997; Constable et al., 2003; EPA, 2004; Paul & Meyer, 2001). For STPs, primary, secondary and tertiary levels of treatment remove varying proportions of nitrogen, phosphorus and other pollutants and reduce the biological oxygen demand of the waste water prior to discharge back into the aquatic ecosystem. Tertiary treatment offers the highest removal of nutrients with removal efficiency up to 90% of P, whereas lagoon treatment can achieve removal efficiencies of 90% biological oxygen demand, 75% suspended solids and 30% phosphorus under optimal conditions (Freedman, 1995; Kang et al., 2008). However, sewage lagoons rely on long holding time (typically months) for biological degradation to occur; heavy or sustained precipitation events can result in the discharge of partially treated sewage water (Davies-Colley et al., 1995; Paul & Meyer, 2001). Discharge of lagoon waste water may be influenced by precipitation events when inflow exceeds holding capacity or the population being served exceeds the lagoon capacity (Carpenter et al., 1998; Cunha et al., 2011; EPA, 2004; Kang et al., 2008). It is important to identify the factors that influence the treatment of wastewater as the effects of its discharge may contribute to eutrophication of rivers. Thus, for point sources such as STPs, the type of treatment and level of waste water treatment can influence in-stream nutrient forms and concentrations, and has a role in the temporal variation of nutrients due to point sources (Alexander et al., 2008; Cunha et al., 2011; Davis-Colley et al., 1995).

The GLWQA (1972) has led governments of Canada and the USA towards understanding and identifying non-point sources and point sources since the 1970's when anthropogenic activities were first linked to the degradation and eutrophication of Lake Erie and the Great Lakes basin (The Government of Canada, Environment Canada, 2012). Through the identification of agriculture and STPs as non-point sources and point sources, respectively, mitigation actions were initiated and focused on treatment of wastewater and land management practices (The Government of Canada, Environment Canada, 2012). However, with a return of algal blooms to and degrading water quality of Lake Erie, reassessment of non-point sources and point sources is required to understand the cumulative impacts of land use on water quality in the Great Lakes basin.

Past studies have shown that the spatial scale used to describe land use influences the relationship between land use and stream nutrient concentrations (Dodds et al., 2008; Hunsaker & Levine, 1995; Iniguez-Armijos et al., 2014; Richards et al., 1996). Previous studies have found that the increasing proportions of agriculture and urban at the catchment scale are significantly and positively correlated with stream nitrogen and phosphorus concentrations (Allan et al., 2004; Carpenter et al., 1998; Omernik, 1977). For example, Banner et al. (2009) demonstrated that the concentration of total phosphorus was significantly associated with the proportion of cropland in the riparian zone in streams located in Kansas. Similarly, vegetated riparian buffers have been shown to significantly reduce the transport of nutrients to rivers by assimilating nutrients into plant tissues and also by acting as barriers between the landscape and stream during overland and runoff flows (Dodds & Oakes, 2008; Iniguez-Armijos et al., 2014; Sardans et al., 2013). These studies suggest that land use proximal to the stream can disproportionately influence nutrient retention on (or loss from) the land and thus the amount of nutrients and sediment transported to the stream. As such, studies of stream water quality should quantify land use at multiple spatial scales to ensure all key relationships between land use and stream quality are captured.

Linear regression models have been successfully used to describe relationships between water quality parameters and land use (Dodds et al., 2004; Dodds and Oakes, 2008; Jones et al., 2001; Pratt & Chang, 2012). The utility of regression models as predictive tools, however, is dependent on the ability of the model to successfully predict under different spatial and temporal scenarios (Arhonditis et al., 2004). Although many studies have identified significant relationships between land use and water quality, only a few have evaluated the performance of their models and the utility of the model remains uncertain (Arhonditis et al., 2004). Multiple metrics have been used to evaluate model performance and assess model accuracy (Archonditis et al., 2004; Nash & Sutcliffe, 1970; Willmott & Matsuura, 2006, Willmott et al., 2012, Wright et al., 2000). For example, disagreement statistics are used to identify the amount of error between the observed and expected concentrations and enable comparison of a models performance among evaluation scenarios. Conversely, site observed:espected (O:E) scores evaluate the similarity between observed and predicted nutrient concentrations and identify model performance based on individual site success (Wright et al., 2000) . The Nash-Sutcliffe Efficiency Index (Ef) assesses the overall accuracy of a model by determining how well the plot of the observed and expected data fit the derived models 1:1 line (Nash & Sutcliffe, 1970; Willmott et al., 2012). The Ef determines if the model accurately predicts the expected value compared to the observed value (NSE = 1): where if the mean of the training data used to derive the model is a better predictor of the expected value (NSE = 0) or if the model is a poor predictor of expected concentrations (NSE <1) (Nash & Sutcliffe, 1970; Willmott et al., 2011). Each of these evaluation metrics evaluates how well the model is able to predict in comparison to observed data. The development of models as predictive tools requires that model performance is evaluated to assess the utility of the model as a predictive tool for water quality management.

1.3 Temporal Variation in Stream Nutrient Concentrations

On a landscape scale, vegetation in the form of forest cover in the catchment and the presence of stream side riparian buffers, limit the transport of nutrients and sediment from the landscape to the stream (Carpenter et al., 1998; Dodds & Oakes, 2008; Zhang et al., 2013). Vegetation attenuates nutrients on the land for growth and structural development as well as stabilizes soils through root cohesion, thereby minimizing erosion and transport of sediment bound nutrients to receiving streams (Basnyat et al., 2000; Dodds & Oaks, 2008; Whiles et al., 2000). The importance of vegetation on the landscape has been assessed at a catchment scale, as well as for riparian zones, in both cases decreasing transport of sediment and nutrients to the stream (Paul & Meyer, 2001; Dodds & Oakes, 2008). The positive effects of vegetation for nutrient retention have also been observed in restoration projects where the effects of restoring natural vegetation cover through the conversion of row crops to grasslands has been associated with reduced nutrient loads to receiving waters (Schilling & Spooner, 2006). However, vegetation condition varies temporally and thus describing vegetative growth phases (emergent, active, senescent and dormant) may provide a more thorough understanding of its influence on temporal variation of in-stream nutrient concentrations.

GIS and remote sensing allow exploration of the relationship between vegetation and water quality as satellite imagery can quantify temporal variation of vegetation structure due to climate and environmental stressors. The Normalized Difference in Vegetation Index (NDVI) (USGS, 2010) quantifies vegetation greenness across multiple spatio-temporal scales producing a greenness value that describes the vegetation condition of a catchment. This greenness index can be used to capture temporal changes and to understand how the lifecycle of vegetation influences water quality (Griffith et al., 2002; Singh et al., 2013). Previous studies (Basnyat et al., 2000; Griffith et al., 2002; Singh et al., 2013) have used a single time period classification of the landscape from satellite imagery and average water chemistry to explain the association between NDVI and nutrient concentrations. However, by incorporating temporally matched NDVI and water chemistry, our understanding of the spatial and temporal variation of in-stream nutrient concentrations in catchments may be improved.

2 Research Goals and Hypotheses

2.1 Research Goals

The overarching goal of this thesis was to quantify the cumulative influence of spatial patterns in land use and land cover on the temporal variation of nutrient concentrations in tributaries of the Great Lakes. To achieve this goal, two sub-goals were defined.

1. Assess the association between catchment scaled vegetation conditions and stream nutrient concentrations and describe how the strength and nature (direction) of this association varies among seasons.

Sub-goal 1 was achieved by completing the following objectives:

a) Collect grab samples from 29 Great Lakes tributary sites over 10 sampling time periods between May and November, 2012. Samples were analyzed for concentrations of seven forms of nutrient: ammonia (NH_3), total Kjeldahl nitrogen (TKN), nitrate and nitrite (NO_3- + NO_2-), nitrogen (TN), soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), and total phosphorus (TP).

b) Describe catchment wide vegetation condition using the Normalized Difference in Vegetation Index (NDVI)(USGS, 2010) for the 29 water quality sites for times coinciding with the 10 water sampling periods.

c) Determine the relationship between vegetation condition and nutrient concentrations at the 29 sites for each of the individual water sampling periods using ordinary least squares regression analysis (OLS) (Figure 2.1A).

d) Identify trends in the relationships between seasonal greenness and nutrient concentrations (Figure 2.1B). These trends represent 'critical periods' of vegetation condition that are related to nutrient concentrations in stream waters.

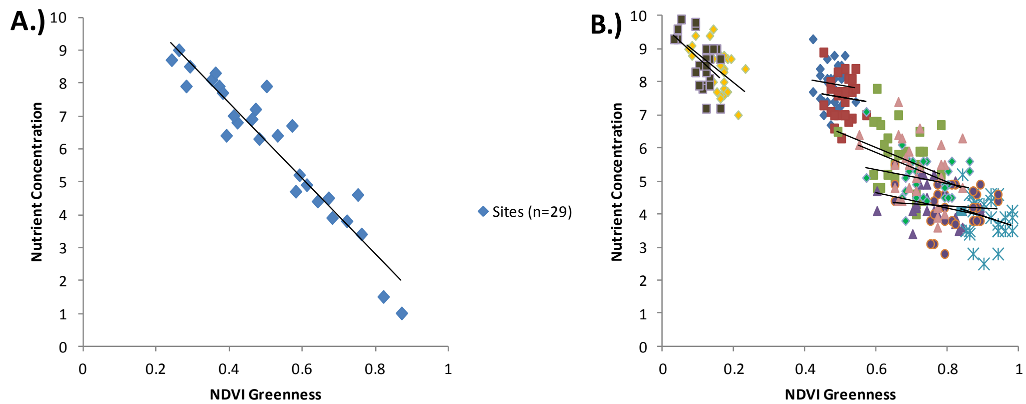

Figure 2.1: Scatterplot describing the association between hypothetical site nutrient concentrations and catchment greenness (A). Each point represents a sample site. Using linear regression a model will be created to identify trends in nutrient concentration associated with 10 sampling periods (*). A comparison will be made between the 10 hypothetical time points (B) relating greenness to stream nutrient concentrations in south western Ontario (SWO). Each line represents a sample time that we will use to identify trends in the seasonal variation of nutrient concentration related to greenness.

2. Identify the drivers of the relationship between human activities and stream nutrient concentrations for water quality parameters collected from May through November in 2012.

Sub-goal 2 was achieved through the following objectives:

a) Collect water grab samples from 29 Great Lakes tributary sites during 10 sampling periods between May and November 2012. Samples were analyzed for concentrations of seven nutrient forms: $NH_{3,}$ TKN, NO_{3^-}+NO_{2^-}, TN, SRP, TDP, and TP.

b) Describe catchment wide human activity gradients (HAGs) of non-point sources, including land use (i.e., proportion agriculture, proportion urbanization), land use within 30 m buffer of headwater streams (Strahler order 1 & 2), and land use buffering (30 m) a 600 m river segment above each of the 29 sampling sites.

c) Describe HAGs of point sources using STP data expressed as density of population served for STPs and lagoons per km^2 (STP-persons), the volume of effluent discharged from the STP (STP-effluent) and the distance upstream to nearest STP or lagoon (STP-distance) for each of the 29 sampling sites.

d) Generate a model from multiple ordinary least squares linear regression to compare the nature and shape of relationship between HAGs and in-stream nutrient concentrations for critical vegetation periods identified in sub-goal 1.

e) Assess the cumulative influence of quantified land use descriptors on stream nutrient concentrations using multiple regression analysis for critical vegetation periods identified in sub-goal 1.

f) Evaluate the predictive performance of my nutrient models outside of the spatial and temporal bounds for which they were created using statistical measures of disagreement and agreement

g) Inform policy makers of the use of catchment wide land management to mitigate stream nutrient concentrations through knowledge gained on the drivers of nutrients and how these drivers vary among seasons for tributaries to the Great Lakes.

2.2 Hypotheses

I hypothesize that:

1.) There will be an inverse relationship between greenness and nutrient concentrations for all sampling periods, such that for time periods where vegetation is actively photosynthesizing and greenness values are high (predicted to be during the active phase) nutrient concentrations will be lowest. During this active growth phase, vegetation will assimilate nutrients and water, thereby limiting nutrient loss, runoff and seepage that would transport nutrients to the stream.

2.) The slopes of the regression models will explain temporal variation in nutrient concentrations thereby identifying critical periods of vegetation greenness that are associated with seasonal variation in stream nutrient concentrations. The critical periods identified will be defined as the emergent, active, senescent and dormant phases of vegetation growth, similar to 'growing days and brown days' (Figure

2.2) as described by Griffith et al., 2002. The dormant period slopes will be greatest, and emergent and senescent period slopes will be moderate. As vegetation condition and greenness will peak in the active period, slope values will be lowest.

3.) Proportion agriculture, urbanization and STP population served will have positive linear relationships with nutrient concentrations in 29 catchments in southwestern Ontario (SWO). Upstream distance to STP will have a negative relationship with nutrient concentrations due to downstream dilution of effluent with stream water..

4.) Variation in stream nutrient concentrations in the dormant period will be driven by agriculture and urbanization due to the increased mobilization and transport of sediment and nutrients due to rainfall and runoff events.

5.) Variation in stream nutrient concentrations in the emergent and senescent periods will be cumulatively affected by non point (agriculture and urban) and point sources (STPs) as the buffering effects of vegetation are more limited.

6.) Variation in stream nutrient concentrations in the active period will be driven by point sources such as the population served per km^2 by an STP due to vegetation reaching its growth maximum and thus achieving the greatest buffering capacity.

7.) Model predictive performance will be strongest under the data quality scenario and under the temporal scenario that is most similar to the climate conditions of sampling season from which the nutrient models were derived due to regional similarities in physiographic and climate conditions

8.) Model performance will be weakest outside of the spatial bounds used to derive the model and under climate conditions dissimilar to those used to derive the nutrient models.

9.) The predictive performance of the nutrient models will be greatest during the dormant and senescent periods when land use drivers are most active due to the lack of vegetation and an increased opportunity for the transport of nutrients via through flow and runoff from the landscape to the stream.

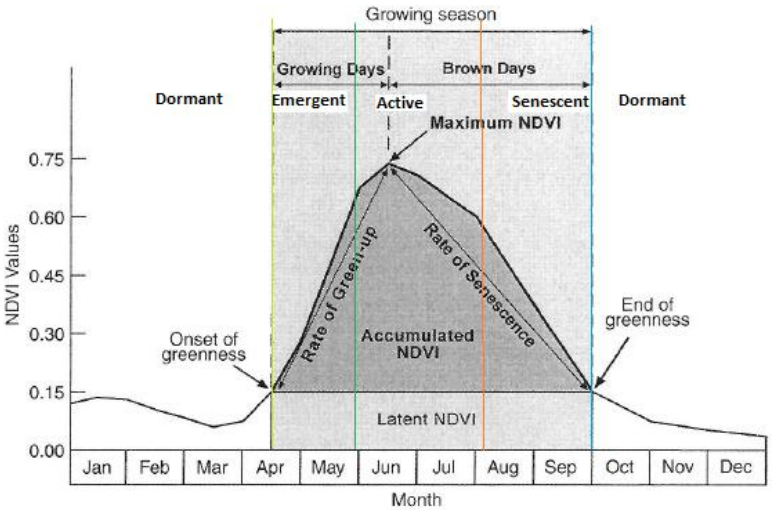

Figure 2.2. Vegetation Phenology curve metrics from enhanced AVHRR imagery from Griffith et al. (2002) illustrating the temporal response of vegetation in the Great Plains (after Reed et al., 1994). Emergent, active, senescent and dormant periods of vegetation are noted as labelled above. The emergent period is represented by the onset of greenness and increasing NDVI values. The active period is represented by high NDVI values and highest greenness. Senescence is associated with the browning of vegetation and decreasing greenness. The dormant period, which extends from October through April, is associated with below latent NDVI values. (Adapted from Griffith et al., 2002)

3 Methods

3.1 Study Area

Twenty-nine lower Great Lakes catchments (area range 106 - 571 km^2) were identified in the mixed-wood plains ecozone (Crins et al., 2009) across Southern Ontario (Figure 3.1A). Regional climates are classified as humid and temperate with annual temperatures ranging from 4.8^{o}C to 9.4^{o}C and seasonal temperatures exhibiting moderate variability (mean temperature; May 17^{o}C - 20^{o}C, July 25^{o}C - 28^{o}C, October 13^{o}C - 16^{o}C; Crins et al., 2009). The mean length of the growing season ranges from 205 - 230 days with annual precipitation ranging from 720 - 1000mm. Precipitation is evenly distributed throughout the year, ranging between 67-99mm per month (Crins et al., 2009). Regional river basins drain into Lake Huron, Lake Erie or Lake Ontario and are characterized by glacial deposits with predominately glacial till and silt substrate (Crins et al., 2009; Yates & Bailey, 2010a). Oak savannah woodlands, on the eastern coast of Lake Huron, and Carolinian Woodlands on the north shore of Lake Erie towards Lake Ontario, typified the vegetation of the area prior to the 19th century. Since then settlements have transformed woodlands into agricultural fields dominated by small grains, corn, soybean, and hay crops. The Ministry of Natural Resources classified the dominant land cover in the region, by area, as cropland which comprises 57% of agriculture land use (Crins et al., 2009). Populations for major urban centers in the region include London (366,151), Kitchener (219,153), Cambridge (126,748), and Waterloo (98,780), and are experiencing population growth ranging from 1.0% to 7.1% between 2006 and 2011 (Statistics Canada, 2011). Smaller centers (i.e., population < 50,000) include Stratford, St. Thomas and Woodstock (population growth 1.2% - 5.4%). Smaller communities outside major urban centers, such as New Hamburg (11,953) and Drayton (1,880), exhibit the largest population growth rates in the region at 15.9% and 11.1%, respectively (Statistics Canada, 2011). Wastewater management infrastructure for the larger urban centers consists of mechanical treatment, whereas in rural communities or smaller urban centers wastewater is managed through wastewater lagoons that discharge effluent seasonally..

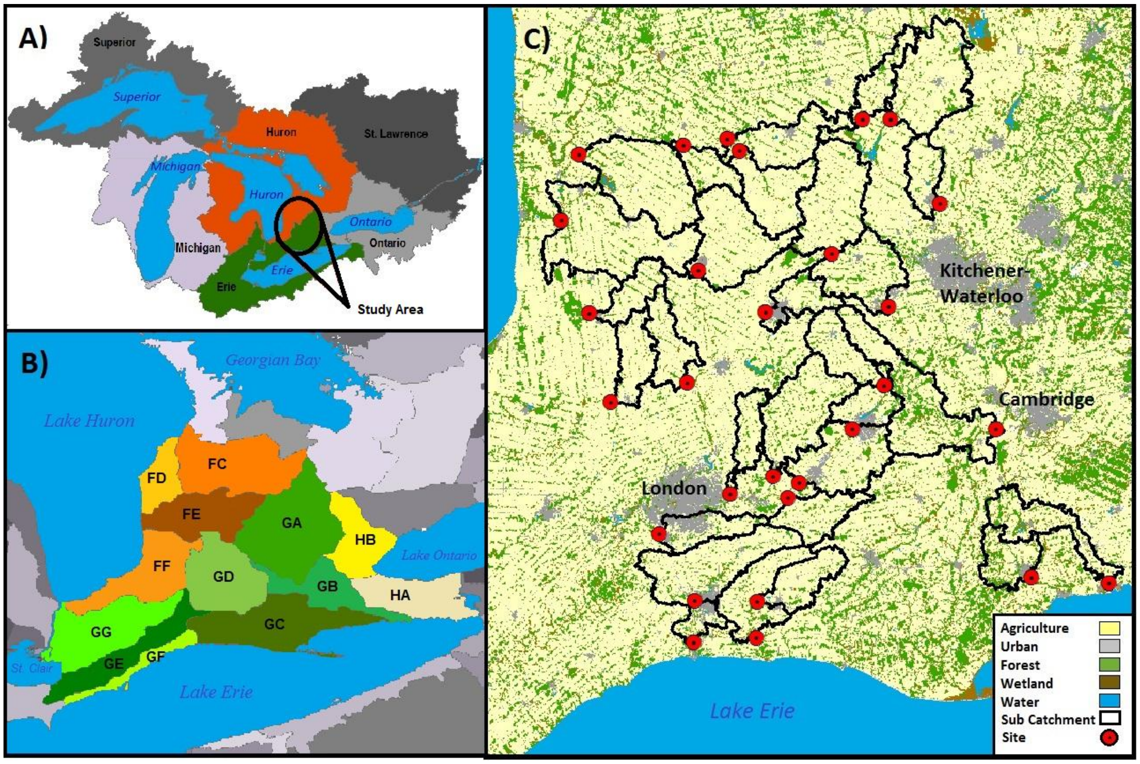

Figure 3.1. A) Location of study area (black circle) in relation to Great Lakes watershed boundaries for tributaries of Lake Huron (orange), Lake Erie (green) and Lake Ontario (yellow). B) Location of the National Hydro Network watershed subunits draining into Lake Huron (orange shades), Lake Erie (green shades) and Lake Ontario (yellow shades). C) Location of the studied catchments for 29 selected Ontario Provincial Water Quality Monitoring Network sites (red circles) included in the study. Proportion of agriculture (yellow) and urban development (grey) in southwestern Ontario are indicated for each study catchment (black polygons).

3.2 Site Selection

Sites were selected using nine criteria based on historical data availability Provincial Water Quality Monitoring Network (PWQMN), catchment size, land use and physiography (Table 3.1). First, a list of 2149 potential sites was established that consisted of all river sites monitored by the PWQMN in the province of Ontario. Second, we identified watersheds draining into Lakes Huron, Erie and Ontario including the Thames, Grand, Ausable Bayfield, St. Clair, Saugeen, Kettle Creek, Catfish, Long Point, Halton, Hamilton and Niagara drainage areas as outlined by the National Hydro Network Subunits. All 1499 sites outside these boundaries were removed from the candidate list (Figure 3.1B). Third, PWQMN records were examined to identify sites that were sampled between 2002 and 2010, resulting in the retention of 227 candidate sites. Fourth, candidate sites with less than five years of data between 2002 and 2010 were removed reducing the pool of candidate sites to 194. Catchment boundaries for the remaining 194 sites were delineated using ArcGIS 10.0 (ERSI 2010a) extension Arc Hydro 2.0 (ESRI, 2010b). Delineation was based on NASA's Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) Digital Elevation Model (DEM) imagery and the National Hydro Network stream layer for Southern Ontario and the 194 site location coordinates. Fifth, variation in nutrient export associated with catchment size was controlled by retaining sites with catchments areas >100 km^2 and <750 km^2 reducing the candidate list to 90 sites. Sixth, among the remaining 90 candidate sites we identified 6 sites that we used as a template to represent physiographic characteristics (i.e., surface geology – described using ArcGIS 10.0 [ESRI, 2010a]) typical of streams draining into Lake Erie. The six template sites were selected because they were being monitored by the Science and Technology Branch of Environment Canada to describe nutrient loads to Lake Erie and represented geology typical of Lake Erie catchments. To identify sites that fit the template set out by these six streams we applied a hierarchical cluster analysis to the 90 sites and identified 52 candidate sites that were grouped with the template sites. The proportion of agriculture and urban land cover in the remaining 52 catchments was described using the Intersect Polygon Raster (isectpolyrst) tool in Geospatial Modeling Environment (2013) to extract land use data from Agriculture and Agri-Food Canada crop inventory maps (30m resolution, AAFC 2012) using the delineated catchment boundaries. Sites were inspected for representation of the greatest variability in land use among the identified catchments as well as for historical dissolved reactive phosphorus and TP data. Seventh and finally, site visits were conducted at each of the 52 final candidate sites to assess site accessibility and potential logistical problems that might be encountered during field sampling and interfere with sampling protocols. Field inspections resulted in the selection of 29 sites that represented the most complete gradients of agriculture and urban development but also met logistical requirements. The selected 29 sites were located in eight watersheds supplying Lake Huron and Lake Erie. Four watersheds (Grand, Long Point, Kettle, Catfish) drained south into Lake Erie, three watersheds (Ausable, Maitland, Saugeen) drained to Lake Huron and the remaining Thames River watershed drained into Lake St. Clair (Figure 3.1 C). 24 of the 29 sites were identified as independent, whereas the remaining five exhibited nesting.

Table 3.1. Criteria used for selection of sampling sites for GLNI. Site selection criterion incorporated Environment Canada's 6 long term monitoring sites for Lake Erie tributaries into the selection criteria (Filter 6) as model sites. 29 sites were selected for inclusion in this study based on these criteria.

Filter	Criterion	# of Candidate Sites
1	Current or historical site in the Ontario Provincial Water Quality Monitoring Network	2149
2	Located in National Hydro Network Subunits FC, FD, FE, FF, GA, GB, GD, GE, GF, GG, HA or HB	650
3	"Last Record" of sampling occurred in/or between 2002 and 2010	227
4	"Number of Years" sampled was greater than or equal to 5	194
5	Site catchment area greater than 100 km^2 but less than 750 km^2	90
6	In same surface geology cluster as 6 GLNI Lake Erie tributary monitoring sites	52
7	Absence of logistical constraints on sampling	29

3.3 Water Sampling

Water quality sampling was conducted approximately biweekly from May 2012 through November 2012 for a total of 10 water samples per site. Grab water samples were collected in the thalweg at approximately 60% depth and analyzed for major phosphorus (i.e., Total Phosphorus [TP], Total Dissolved Phosphorus [TDP], Soluble Reactive Phosphate/Orthophosphate [SRP]) and nitrogen (Total Kjeldahl Nitrogen [TKN], Total Nitrogen [TN], Ammonia [NH_3], and Nitrate-Nitrite [NO_3^-+NO_2^-] forms. These nutrient forms were targeted as they are known to impact tributary and nearshore water quality and are key limiting nutrients of primary productivity (Allen & Castillo 2007, Carpenter et al. 1998). One high density polyethylene bottle (1L) was collected for field filtration (0.45μm cellulose acetate filter paper) of water into Flint glass bottles (125mL) for analyses of NO_{3-}+NO_{2-}, NH_3, TKN, TDP and SRP. Grab water samples were also collected in sterile 125ml Flint glass bottles for total nitrogen unfiltered (TN) and total phosphorus unfiltered (TP). Samples were stored at approximately 4°C in a cooler and transported overnight to the National Laboratory for Environmental Testing in Burlington, Ontario for analyses (Table 3.2).

Table 3.2. Summary of nutrient analysis methods used by the National Laboratory for Environmental Testing in Burlington, Ontario (CCME, 2009). Filtering of samples was conducted using 0.45µm cellulose acetate filter paper.

Nutrient	Analysis Method	Max. Holding Time
NH_3 (Filtered*)	Automated Continuous Analysis (CFA) Phenate Photometric Method	48 hrs
TKN (Filtered*)	Phenate photometric method through acid digestion	48 hrs or 7 days if acidified
$NO_3^-+NO_2^-$ (Filtered*)	Determined colorimetrically by Azo Dye Photometric methods using a copper cadmium reduction	48 hrs
TN (Un-filtered)	Alkaline Persulfate Oxidation, Automated Flow Injection Analyzer (FIA), Hydrazine Reduction, Azo Dye Photometric Method	48 hrs
SRP (Filtered*)	CFA Ascorbic Acid Reduction-Molybdate Complex, Photometric Method	48 hrs
TDP (Filtered*)	Total Phosphorous, Filtered, Acidic Persulfate Digestion, CFA, Stannous Chloride-Molybdate Complex, Photometric Method	18 days
TP (Un-filtered)	Total Phosphorous, Unfiltered, Acidic Persulfate Digestion, CFA, Stannous Chloride-Molybdate Complex, Photometric Method	18 days

*filtered through a 0.45 um cellulose acetate membrane filter

3.4 Assessing Seasonal Variation in Nutrient Concentration through Vegetation

To assess the effect of landscape seasonality on nutrient concentrations, we evaluated the relationship between terrestrial vegetation condition in the catchment and nutrient parameters for each site using data from the 10 sampling events between May and November 2012. Vegetation condition was quantified for each catchment using the Normalized Difference Vegetation Index (NDVI). Vegetation condition, as indicated by photosynthetic activity, varies throughout the lifecycle of vegetation with emergent and active phases having increasing and high photosynthetic activity whereas dormant and senescent phases exhibit declining or low to no photosynthetic activity (Griffith et al., 2002, Reed et al., 1994). The change of state of NDVI between sample times may be associated with a change of state in nutrients indicating nutrient attenuation on the land during growth phases of vegetation. Moderate Resolution Imaging Spectroradiometer (MODIS; 250 m resolution) was obtained for each of the 10 sampling events within 8 days of each sampling date to account for the temporal variability of vegetation condition during the 2012 sampling period. MODIS data was used to calculate the mean normalized difference vegetation index (NDVI) value (-1 through +1) for each catchment. NDVI is calculated by subtracting the red reflectance from the Near Infrared Reflectance (NIR) and dividing this by the sum of the NIR and red reflectance (Equation 1). NDVI values assigned to each pixel (250m x 250m) represent the vegetation condition (greenness) for that pixel and were used to characterize the catchment associated with nutrient concentrations. Pixels classified as no data, poor quality or cloud covered were removed from the analysis using the clip tool in ArcGIS. NDVI and the catchment layer (shapefile) were input in geospatial modelling environment (GME) (Hawthorne, 2012) to calculate mean, minimum, and maximum NDVI for each catchment of which a mean NDVI value was assigned to each catchment studied.

$$\text{NDVI} = \frac{\text{(Near Infrared Reflectance (NIR) - Red Reflectance)}}{\text{(Near Infrared Reflectance (NIR) + Red Reflectance)}}$$

Equation 3.1: NDVI calculation for vegetation greenness and vegetation condition using MODIS satellite imagery with pixel values (digital numbers range from 0-255). (Adapted from Lillisand et al, 2008).

To capture the variation in vegetation condition in each catchment we described NDVI using three metrics. The metrics were used to quantify temporal variability of vegetation condition in each individual catchment for sampling events 1 through10. The first metric was average NDVI for each sampling event (n=10), calculated for each catchment to represent overall vegetation condition in the catchment at the time each water sample was collected. Secondly, Delta (Δ) NDVI was the second metric we used to describe differences in NDVI for each catchment between sampling events. Δ NDVI was calculated from catchment average NDVI from time 1 to time 2 to characterize the differences between the initial state and subsequent state of image NDVI, resulting in nine measurements of catchment NDVI (Equation 3.2A). Differences between subsequent nutrient concentrations were also calculated resulting in nine Δ-nutrients for every catchment. The 9 Δ-nutrient measures were then paired with the Δ-NDVI values. The third and final metric calculated was the $NDVI_{sum}$ that characterized the additive effect of vegetation in the catchment. Catchment pixel values that represented vegetation condition were summed in ArcGIS 10.0 using the *Combinatorial Or* tool in Spatial Analyst resulting in nine new layers of NDVI pixel values (Equation2B). Average catchment $NDVI_{sum}$ was then calculated in GME (Hawthorne, 2012) using the *intersecpolygonraster tool* for the 9 new layers. Nutrient concentrations from samples 2-10 for a total of 9 measures, were used to assess the association between stream nutrients and cumulative NDVI.

Equation 3.2: Normalized Difference Vegetation Index (NDVI) metrics used to quantify changes in NDVI for each catchment. A) Δ-NDVI represents the change in catchment average NDVI between each time and its succeeding measurement for each catchment. Δ nutrient concentration was calculated to assess the association of nutrient variability with NDVI variability. Individual sample times were represented by day(described as $time_{(i)}$) values for NDVI and nutrients. B) $NDVI_{sum(i)}$ represents the additive effect of vegetation for each pixel in the catchment. NDVI pixel values for each sample time were identified by Ti where i represents sample times 1 through 10.

A) $\Delta\ NDVI = NDVI_{129} - NDVI_{161};\ NDVI_{161} - NDVI_{177};\ NDVI_{177} - NDVI_{193}$; etc

where $NDVI_i$ = catchment average NDVI at time i

i represents day of year

Δ Nutrient concentration $= NC_{129} - NC_{161};\ NC_{161} - NC_{177};\ NC_{177} - NC_{193}$; etc.

where NC_i = nutrient concentration at time i

B) $NDVI_{sum(i)} =$

$NDVI_{T1} + NDVI_{T2} = NDVI_{sum(1)}$;

$NDVI_{CF1} + NDVI_{T3} = NDVI_{sum(2)}$;

$NDVI_{CF2} + NDVI_{T4} = NDVI_{sum(3)}$; etc.

where $NDVI_{Ti}$ is the NDVI at sample time i; where i=1-10

and sum(i) is the sum of the NDVI at time i with NDVI at the subsequent time

Linear regression analysis (α = 0.05) was used to independently determine the association between temporal variation in each of the NDVI metrics and the seven nutrient parameters (NO_{3-}+NO_{2-}, NH_3, TKN, TN, SRP, TDP and TP) for each individual catchment. No significant associations ($p>0.1$) were found between nutrient concentration (NO_{3-}+NO_{2-}, NH_3, TKN, TN, SRP, TDP and TP) and the three NDVI metrics for any catchment. Thus, mean nutrient concentrations were calculated for each sampling site using the entire May to November sampling period, hereafter referred to as the 2012 sample season.

3.5 Land Use and Human Activity Descriptions

Land use descriptions were calculated for the 29 sampled catchments based on the boundaries delineated using Arc Hydro 2.0 extension for ArcGIS 10.0 (ESRI 2010b), and a 2012 crop inventory map (30m resolution) obtained from Agriculture and Agri-Food Canada classifying land use across the region. The 2012 crop inventory map was then re-classed using ArcGIS 10.0 (ESRI, 2010a) to produce 6 classes of land use (agriculture, forest, urban, water, wetland/bog/grassland, and no data). Agricultural and urban land uses were described at four spatial scales (Table 3.3):

1. Entire catchment area.
2. 30 m buffer for the entire stream network within the catchment (*sensu* Barton, 1997; Dodds and Oakes, 2008; Griffith et al., 2002;).
3. 30m buffer for headwater streams (Strahler order 1 or 1-2 based on size of catchment) (*sensu* Dodds and Oakes, 2008).
4. 30m buffer extending 600m upstream of the site on the main stem for each catchment (based on median distance to nearest upstream tributary).

Buffers (30m) were produced for all streams within the catchment in ArcGIS 10.0 (ESRI, 2010a). Headwater streams (Strahler orders 1 and 2) were selected for each catchment and a streams polyline shapefile generated. Buffers around the identified 1st and 2nd order segments were then selected for each catchment and a polygon file produced. For the fourth spatial scale a 600m segment of stream upstream from each sampling site was selected. The 600m distance upstream represented the median distance from sample sites to the nearest upstream tributary and accounted for potential effects that tributary streams may have on nutrient concentrations in the main reach of the river (dilution or concentration). A buffer (30m) was applied to the 600m segments to produce a polygon shapefile for each catchment. The proportion agriculture and proportion urban land use in each catchment was determined for each spatial scale using the intersect polygon raster tool (*insectpolyrst*) function in GME (Hawthorne, 2012).

Table 3.3: Acronyms used to represent land use descriptors and STP metrics for each catchment.

Land Use Acronym	Land Use Descriptor
Urb-C	Proportion urban in the catchment
Ag-C	Proportion agriculture in the catchment
Urb-buf	Proportion urban in a 30m stream buffer throughout the catchment
Ag-buf	Proportion agriculture in a 30m stream buffer throughout the catchment
UrbHW	Proportion urban in 30m stream buffer of headwater streams
AgHW	Proportion agriculture in 30m stream buffer of headwater streams
Urb600m	Proportion urban in a 30m stream buffer 600m upstream form the site
Ag600m	Proportion agriculture in a 30m stream buffer 600m upstream from the site
STP-EFFQ	Total effluent discharge from May through November (m^3)
STP-persons	Sewage Treatment Plant population served per km^2 in the catchment
STP-distance	Distance along the river from site to nearest upstream STP (m)

Sewage treatment plant (STP) activities in the 29 study catchments were summarized with three metrics. First, the distance from the site to the nearest upstream STP in each catchment was calculated using the ArcGIS 10.0 *Origin to Destination Cost Matrix* function (ESRI, 2010b). Second, the population served by STPs was calculated for each catchment as an indicator of plant size. Sewage treatment population density was calculated by dividing the population served (represented by 2011 Canadian population census data for each municipality containing a STP) by catchment area. Third, total monthly effluent discharge for each STP was extracted from annual wastewater reports compiled by each facility manager and submitted in accordance with the Environmental Compliance Approval to the Ontario Ministry of Environment and Climate. STP total monthly effluent discharge values were summed to calculate the total volume of effluent discharged for the May through November 2012 sampling period for each catchment (m^3).

3.6 Data Analysis

Descriptive statistics were calculated for all dependent (i.e., water quality) and independent (i.e., land use) variables. The degree of normality was assessed for water quality and land use variables using box plots, z-scores and the Shapiro-Wilk test for normality. All data were transformed to improve normality. Dependent variables (nutrient data) and sewage treatment data (population density and distance upstream) were $\log_{10}(x+1)$ transformed. Agriculture and urban data (watershed, 30 m buffer, headwater streams, and 600m upstream scale) were recorded as proportion of catchment area and were transformed with inverse sine. Pearson correlation analysis (α=0.05) identified multi co-linearity between land use descriptors through the calculation of the variance inflationary factor (VIF) value ($VIF=1/(1-r^2)$) (Levine et al., 2004). A conservative criterion of VIF >5 was adopted to identify predictor variables exhibiting significant co-linearity (Levine et al., 2004).

3.7 Statistical analysis

The statistical program SYSTAT 13 (SYSTAT software, 2009) was used for all statistical analyses. Associations between land use and water chemistry variables were examined using ordinary least squares regression analysis (OLS). OLS regression analysis minimizes the sum of the squared differences between the actual dependent variable and the predicted value of the dependent variable, identifying the magnitude and direction of the relationship between individual nutrient concentrations and land use descriptors (Levine et al., 2004, Zar, 1999). The six predictor variables describing land use in the catchments were entered into the OLS regression model to assess the relationships between land use variables and nutrient concentration. Outliers identified by the OLS regression analysis were removed from the dataset (Outlier = Absolute studentized residual >3.0). OLS regression analyses were run independently for each nutrient variable (NH_3, TKN, NO_{3^-}+NO_{2^-}, TN, SRP, TDP, and TP) to identify significant predictor land use variables (α=0.05), thus generating seven nutrient models. OLS bootstrap re-sampling (10,000 samples) was then used to identify the upper and lower bounds of the standardized coefficients and assess the confidence of the model based on the variance of the explanatory variables (α=0.05).

3.8 Predictive Analysis and Model Evaluation

We assessed the robustness of our nutrient models in predicting average seasonal (i.e., May through November) nutrient concentrations under conditions not captured by our 2012 data. These trial conditions represented three major scenarios. First, we evaluated the ability of the models to predict nutrient concentrations based on nutrient data collected using different, yet comparable, sampling (i.e., number and timing of sample collection) and analytical protocols, hereafter referred to as data quality. Second, we assessed if model performance was spatially robust for novel catchments of similar physiography. Third, because the models were developed solely from 2012 data we assessed model performance associated with the inter-annual variation of nutrient parameters. Temporal evaluation of model performance was conducted under three climatic scenarios (i.e., wet, dry and moderate year) allowing us to identify strengths and limitations of model predictive power associated with differences in annual climate conditions.

For all model evaluations we used PWQMN data to calculate average nutrient concentrations for the sites and time periods of interest. However, because nutrient data collected for our study were collected and analyzed by the National Laboratory for Environmental Testing (NLET) protocols we first compared the NLET and PWQMN protocols to ensure comparability of data collection and analysis for each nutrient parameter. For this assessment Conservation Authorities (CAs) responsible for data collection were contacted to determine the sampling protocol used to collect water samples. Ontario Ministry of the Environment (OMOE) (2006) was contacted to determine analytical procedures for each of the seven nutrient parameters. Based on the resultant information, four criteria were generated that had to be met by the PWQMN data for inclusion in our model evaluation. First, only sites that were identified by CA's to be systematically sampled (versus targeted sampling) were included in the selection process, as our study systematically sampled water quality at 3 week intervals to capture water quality variability. Second, a minimum of 5 samples per site had to be collected within the May – November period to ensure that nutrient variability would be adequately captured for the entire sampling period. Third, of the minimum 5 samples at least 1 sample had to be collected in each season; spring (prior to June 21st), summer (between June 21 through September 20) and fall (after Sept. 21). Fourth and finally, PWQMN methods for sampling and analysis of parameters (NH_3, TKN, NO_{3-}+NO_{2-}, TN, SRP, TDP, and TP) were compared with the National Laboratory for Environmental Testing, Burlington (NLET) to identify any differences in nutrient analysis protocols between programs. Based on this survey, NO_{3-}+NO_{2-}, TP, and SRP were determined to be comparable in terms of the analytical methods used. There were, however, reconcilable differences between TN analyses: PWQMN TKN (unfiltered reactive) and NO_{3-}+NO_2 were summed to give TN which was comparable to TN measured by NLET. TKN was not comparable between the two labs: the PWQMN method included both dissolved and particulate forms whereas the NLET method was for only dissolved forms. Ammonium (PWQMN) was also found not to be comparable to NLET ammonia due to differences in analysis and was not included in model validation. Total dissolved phosphorus was not included in PWQMN sampling protocol and thus was excluded from model evaluation.

3.9 Model Evaluation Site Selection

Sites were selected for each of the model evaluation scenarios using specific sets of criteria designed to identify sites that captured the range of variability in the condition of interest, yet were as consistent as possible in all other characteristics.. For our study, model evaluation was defined as the assessment of a models predictive power using data outside of the spatial, temporal and data quality bounds for which it was created. Predictive power refers to the accuracy of the prediction when comparing PWQMN observed nutrient concentrations to model predicted nutrient concentrations and was used to assess model performance.

3.9.1 Protocol Validation Sites

To assess the effects of analytical protocol differences between the PWQMN and NLET on model performance, we examined the 29 sampled sites for independence and identified 24 candidate sites as not being nested. Second, PWQMN data from 2012 was queried to identify data available for the 23 remaining sites. Limitations in data availability resulted in 13 sites for assessment of analytical protocol between PWQMN and NLET. Average nutrient concentrations (NO_3^-+NO_2^-, TN, SRP, TP) were calculated from the PWQMN data for the May through November sampling period. The PWQMN average values were then compared with expected nutrient concentrations (NO_3^-+NO_2^-, TN, SRP, TP) calculated using the OLS regression models to assess the effects of analytical protocol on model performance.

3.9.2 Spatial Validation Sites

To assess the spatial robustness of model prediction we identified novel sites with similar physiographic characteristics as the sites for which we built our models from. We identified 23 novel sites that did not pass criterion 6 of our original site selection process, and thus were not sampled as part of our study (Table 3.1). Catchments were delineated for each of the 23 candidate sites to identify boundary overlap within the 29 sampled streams. 5 of the 23 sites were found to be nested to some degree with the 29 sampling sites. These overlapping sites were removed resulting in 17 candidate sites for spatial validation. For the 17 candidate sites PWQMN data were queried to identify sites limited by data availability. 10 of the 17 sites were determined to have sufficient data to allow calculation of observed nutrient concentrations for the 2012 May through November sampling season (minimum 5 samples representing all seasons). To ensure the proportion of land use activity for each of the validation catchments were similar to the bounds of the data used to generate the models, agriculture and urban land use proportions were calculated from Agriculture and Agri-Food Canada crop inventory map (AAFC, 2012) using the intersect polygon raster tool in GME (Hawthorne, 2012). STP population served (per km^2) for each catchment was described by census population data (2011). These land use descriptors were then entered into the derived OLS regression models (SRP, TP, NO_3^-+NO_2^-, TN) and the expected nutrient concentrations calculated for each of the 10 spatial validation sites.

3.9.3 Temporal Validation Sites

To assess the nutrient model robustness in predicting inter annual variation of nutrient concentrations, we set out to identify years between 2002 and 2011 with climatic conditions that were both comparable and contrasting to our 2012 sampling year. Inter-annual variation in climatic characteristics can influence water quality parameters limiting the models ability to predict nutrient concentration under different conditions. We used 4 environmental characteristics to identify years of distinct climatic conditions: total precipitation, average daily temperature and average daily discharge for the Thames and Grand River. Precipitation and temperature data were obtained from the London, Ontario, Climate Station for 2002 through 2012 (Environment Canada, 2014) to calculate averages for the May through November sampling period. London climate station data was accepted as the most central climate station in the study area containing the most complete climate record for 2002 to 2012. However, based on preliminary analysis of the collected data, average daily temperature was excluded from the analysis due to low variation among years (mean=14.96; SD=0.64; CV=0.043). Hydrometric stations monitored by Water Survey Canada were also selected to calculate average daily discharge for the May through November sampling period for 2002 through 2012. The upper Thames River and Grand River are the two largest catchments in the study region and were used as surrogates to represent average monthly discharge in the study area. Hydrometric stations were situated approximately at the mid-point of the upper Thames River near Thorndale (Station 02GD015) and on the Grand River at West Montrose (Station 02GA034). Both hydrometric stations were upstream of major urban centers and more than 10km downstream from dams along the main reach of the river to minimize the effects of flow regulation on river discharge. K-means cluster analysis was then run using precipitation and discharge data to group years into 3 clusters based on inter annual differences in climate and associated runoff and flow conditions. Results of the analysis indicated that cluster 1 contained mid-range values for the precipitation and discharge variables and was categorized as moderate climatic years (Table 3.5). Cluster 2 exhibited the highest values for precipitation and discharge of the three clusters and was classified as wet years. Precipitation and discharge values for Cluster 3 were the lowest by approximately two-fold when compared to discharge and precipitation data from cluster 1 and cluster 2. Thus, the years in cluster 3 were classified as dry years. Cluster 3 included our sample year, 2012.

Table 3.4 Results from K-means cluster analysis classifying years based on climate and discharge averages for the May through November sample season (mean (SD)). The mean and standard deviation for precipitation and discharge data associated with each cluster were used to identify dry, moderate and wet years.

Variable	Cluster 1	Cluster 2	Cluster 3
Total ppt.	554.625 (31.177)	714.267 (36.654)	435.275 (40.944)
Thames Q_{Ave}	11.109 (3.319)	12.875 (4.799)	5.451 (2.753)
Grand Q_{Ave}	11.098 (0.837)	10.693 (0.424)	6.248 (1.517)
Years identified	2003, 2004, 2008, 2009	2006, 2010, 2011	2002, 2005, 2007, 2012
Classification	Moderate	Wet	Dry

Specific sites for evaluation of model robustness to variation in annual climatic conditions (i.e., wet, moderate and dry) were selected from the 29 sampling sites based on independence (i.e., sites were not nested with other sites) and sufficient historical data for analysis. The independence criterion removed 6 of the sampling sites from consideration. Examination of PWQMN data of the 23 independent sites was then conducted to identify sites that were monitored between 2002 through 2011. To ensure comparability in assessments of model performance among climatic conditions we only selected sites that had sufficient data available for evaluation in a wet, moderate, and dry year. From this datasheet we identified 2002, 2007, 2008, 2010 and 2011 to have corresponding sites. To choose which years would be included in the evaluation we identified the most consistent list of sites representing wet, dry and moderate years. 2007, 2008 and 2011 were identified as having the most common sites for assessment (n=14). Mean observed nutrient concentrations for NO_3^-+NO_2^-, TN, SRP, and TP were then calculated using PWQMN data from the May through November sampling period. Land use descriptor data was calculated using Agriculture and Agri-food Canada crop inventory map for 2011(AAFC, 2011) for the catchments of the 14 selected validation sites using the intersect polygon raster tool in GME (Hawthorne, 2012). Agriculture and urban activity for each catchment was generated from the 2011 Agriculture and Agri-Food Canada crop inventory maps for all three validation years (2007, 2008 and 2011). 2006 Canadian population census data was used to calculate population density served by STP for each catchment for the 2007 dry and 2008 moderate years. The 2011 census population data was used to calculate STP population served (per km^2) for the wet year (2011). Land use descriptors for all 14 sites had values within the bounds of the 2012-based models. Finally, expected values of NO_3^-+NO_2^-, TN, SRP, and TP for each site for 2007, 2008 and 2011 were calculated by entering the associated land use data into our 2012 models.

To assess model performance we compared nutrient concentrations predicted by the models with nutrient concentrations calculated from PWQMN data. Statistical evaluation measures of disagreement and agreement were used to assess the model's goodness of fit under the five scenarios; data quality, outside of the spatial bounds of the training data, dry, moderate and wet climate conditions. Summary measures of observed and modelled nutrient concentrations were reported as observed and expected average nutrient concentration and standard deviation. Traditional measures of disagreement were the Mean Absolute Deviation (MAD), Mean Square Error (MSE), and the Root Mean Square Error (RMSE). Two agreement measures were also used to evaluate model performance.

MAD was used to measure variability as the average difference of the expected value from the observed mean (Willmott, 1982; Zar, 1999). Mean absolute deviation (MAD) measures the average of the difference between the average absolute error and the absolute error for evaluation sites specific to each scenario and identifies the error dispersion about the mean of the error between observed and expected values. Large MAD was a result of large errors between observed and expected values. Comparatively, MSE measures the average of the sum of error between observed (O) and expected (E) squared. MSE is a weighted metric that can be inflated when large errors exist between observed and expected values. MAD to MSE values were compared between evaluation scenarios to identify when large error existed between observed and expected values for individual cases. As MSE is a weighted metric, if individual cases have large error then the MSE will increase disproportional to the MAD. RMSE is the measure of disagreement typically employed for evaluation of model performance. RMSE is the square root of the MSE and is representative of the standard deviation of the error between observed and expected values (Willmott, 1982). Similarly, RMSE is also a weighted metric that is inflated by large errors for individual cases. RMSE is used to compare model prediction power between models, RMSE can also be used as an accuracy measure for overall model performance (Willmott, 1982; Zar, 1999). MAD, MAE and RMSE are all dimensional measures of disagreement and thus measure the average magnitude of the predictive errors. Therefore, the closer to zero these values are the lower the disagreement between observed and expected datasets (Cook, 1982, Levine, 1999, Willmott, 1985).

The average of the average May through November nutrient concentration and its standard deviation ($\bar{O}(s)$) was compared to the average of the average May through November expected concentration and standard deviation ($\bar{E}(s)$). The overall $\bar{O}$:$\bar{E}$ identified over or under prediction of the nutrient model as well as the dispersion of concentrations for evaluation sites under each scenario.

The two agreement measures, the Nash Sutcliffe Efficiency Index (Ef) and site O:E score were also used to evaluate the similarity between the observed and predicted values. These two statistical approaches have been applied in hydrology, water quality modelling and bioassessment (Archonditis et al. 2004; Nash & Sutcliffe, 1970; Willmott, 2012; Willmott, 2011; Willmott, 2005; Wright, 2000). For these measures, as with all model evaluation approaches, observed values are assumed to be error free. However, when compared to the traditional statistical approaches, Ef and O:E treat the observed values as reference for comparison with predicted values generated by the model. The Nash-Sutcliff test was used to evaluate the predictive power of the 2012 nutrient models (NO_3^-+NO_2^-, TN, SRP and TP). The Nash-Sutcliffe Efficiency Index is a normalized statistic used in hydrologic modelling that determines the goodness of fit of predicted values compared to observed values (Equation 3.3). Predicted nutrient concentrations were calculated using the OLS regression models and associated land use data as described above (*Model Sensitivity* section) and plotted against the observed nutrient concentration to determine the relative magnitude of the residual variance compared to the variance within the observed data (Willmott et al., 2012). The result is an efficiency index that ranges from +1 to - infinity. An Ef values closer to 1 indicates that the modelled data matches the observed data whereas, an Ef value close to 0 indicates the model predictions are as accurate as the mean variance within the observed data and an Ef below 0 indicates the models inaccuracy and poor predictive capacity (Krause et al., 2005; Nash & Sutcliffe, 1970).

Equation 3.3. Nash-Sutcliffe Efficiency Index used for assessing the goodness of fit for hydrologic models. Where Ef = the Efficiency Index, n = sample size, E = the expected value of the dependent variable, O =the measured value for the dependent variable, Ō = the mean of the observed/measured value for the dependent variable.

$$Ef = 1 - \frac{\sum_{i=1}^{n} (O_i - E_i)^2}{\sum_{i=1}^{n} (O_i - \bar{O})^2}$$

(Adapted from Klause et al. 2005)

The final evaluation measure used to assess model performance is the site O:E score. The site O:E score is a metric that examines individual site performance under each of the scenarios by comparing the observed value to the predicted value to determine the prediction power of the model. For evaluation sites that exhibit complete agreement between observed and expected nutrient concentrations the site O:E score will be 1.0. Successful prediction was achieved when site O:E scores fell between the cut off values as derived from River Invertebrate Prediction and Classification System (RIVPACS) General Quality agreement and Environmental Quality Index and designed to define the boundaries of acceptance for O:E (Wright et al., 2000). The cut off values for Site O:E scores were ±0.20 around the O:E = 1.0 with individual sites having an O:E score between 0.8-1.2 classified as successfully predicted. The General Quality Agreement encompasses 6 grades with boundary limits that represent the average risk of assigning a grade that is too low. We assumed an average risk of 20% error in comparison to the General Quality agreement for Environmental Quality Index N-Taxa, where and O:E ≥0.85 receives a grade of 'Very Good' compared to the General Quality agreement for Environmental Quality Index Average Score per Taxon where an O:E ≥0.77 receives a grade of 'fairly good' (Wright et al., 2000). The benefit of the site O:E scores is the ability to identify model over prediction or under prediction at specific sites. Sites that are consistently over or under predicted can be further assessed to identify factors such as land use or management practices that may be further driving nutrient concentrations. Furthermore, we calculated the percent of sites that are successfully predicted (O:E=0.8>1.0<1.2) under each scenario to identify the percent success for evaluation of the overall model performance.

4 Results

4.1 Average Nutrient Concentrations

Average concentrations of all measured nutrient parameters demonstrated substantial variation among the 29 studied rivers (Figure 4.1). On average NH_3 comprised 1% of TN and exhibited the highest variability among all nutrient forms (CV=1.131) compared to TKN, which comprised 14% of TN and demonstrated the least amount of variability among nitrogen forms (CV=0.292) (Table 4.1). Average NO_3- + NO_2- comprised the remaining 86% of TN. TN was, on average, 60 fold greater than TP for the 29 studied rivers (Table 4.1). Average SRP demonstrated the greatest variability among phosphorus forms studied (CV=0.914) and on average comprised 73% of TDP for the 29 sites (Figure 4.1). On average the majority of TP was comprised of dissolved phosphorus forms, indicating that approximately 40% of TP was comprised of particulate forms of phosphorus. TP was identified as the least variable form of phosphorus studied (CV=0.575) (Table 4.1).

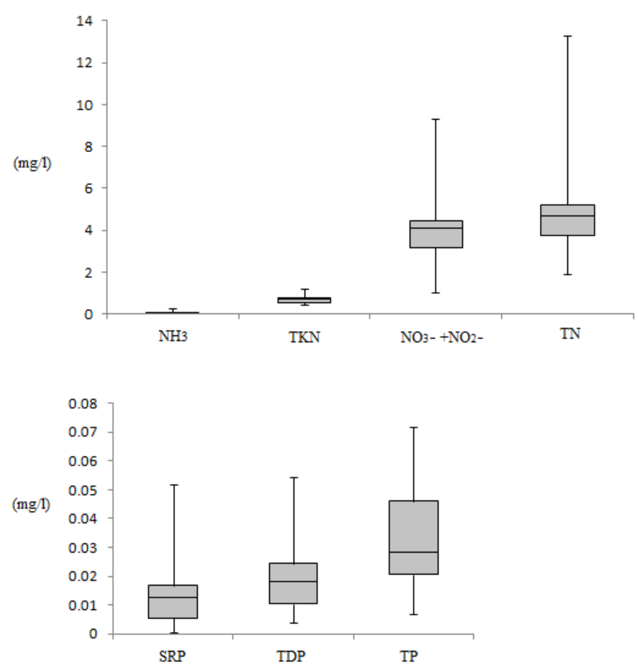

Figure 4.1. Box plots of average concentrations of nitrogen and phosphorus forms sampled 10 times at 29 sites from May through November of 2012. Error bars indicate maximum and minimum average concentrations, the upper and lower bounds of boxes represent 25th percentile and 75th percentile and line bisecting box indicates average of average concentrations of the 29 rivers.

Table 4.1. Descriptive statistics for average concentrations of seven nutrient parameters sampled 10 times at 29 sites in southwestern Ontario from May through November, 2012.

Variables	Median	Mean	SD	CV	Min	Max
NO_3NO_2 (mg/L)	4.078	4.209	1.885	0.448	1.009	9.672
NH_3 (mg/L)	0.029	0.052	0.059	1.131	0.013	0.277
TKN (mg/L)	0.679	0.699	0.204	0.292	0.418	1.254
TN (mg/L)	4.671	4.968	2.352	0.474	1.847	13.789
SRP (mg/L)	0.029	0.035	0.032	0.914	0.001	0.127
TDP (mg/L)	0.043	0.048	0.033	0.682	0.009	0.133
TP (mg/L)	0.067	0.081	0.046	0.575	0.016	0.179

4.2 Temporal Variation of Vegetation Condition

Average vegetation condition of catchments varied temporally throughout the May through November sampling period for the 29 study sites (Figure 4.2). NDVI values increased from May ($NDVI_{129}$) through the beginning of June ($NDVI_{177}$) during the emergent phase of vegetation growth (Table 4.2). Average NDVI values plateaued in June during the active phase of vegetation growth and then declined in NDVI from August ($NDVI_{257}$) through November ($NDVI_{321}$) representing the senescent phase of vegetation. NDVI peaked in July and demonstrated the lowest variability among sample times ($NDVI_{225}$=7386; CV=0.04). November demonstrated the lowest average NDVI ($NDVI_{321}$=3983; CV=0.09) among the May through November sample times. The greatest variability of catchment NDVI was identified in September ($NDVI_{289}$, CV=0.11). Although NDVI captured the intra-annual variation in vegetation condition for the 29 rivers studied, none of the three metrics describing NDVI were significantly associated with nutrient concentrations (NO_3- + NO_2- , $NH_{3,}$ TKN, TN, SRP, TDP, or TP) (Appendix B, C & D).

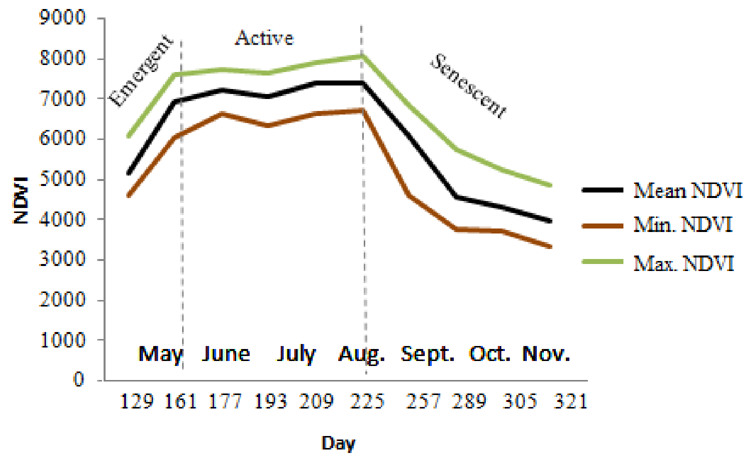

Figure 4.2. The temporal variation of vegetation described by the average Normalized Difference Vegetation Index (NDVI) for the 29 study catchments over the May through November sampling period.

Table 4.2. Descriptive statistics for land cover metric NDVI measured in 29 catchments in southern Ontario.

Day	mean	SD	SE	CV	min	max
129	5165	364.76	67.73	0.07	4598	6098
161	6914	341.94	63.50	0.05	6037	7611
177	7211	272.52	50.60	0.04	6610	7739
193	7045	356.89	66.27	0.05	6350	7663
209	7382	357.23	66.34	0.05	6645	7896
225	7386	296.40	55.04	0.04	6706	8055
257	6063	514.36	95.51	0.08	4586	6848
289	4557	513.65	95.38	0.11	3745	5729
305	4298	351.69	65.31	0.08	3697	5254
321	3983	349.31	64.86	0.09	3352	4872

4.3 Land Use Descriptors

Assessment of the land use descriptors identified that the proportion of agriculture (60.9% - 91.9%) and urban activity (0.5% - 27.5%) varied substantially among the 29 rivers studied. Comparing the 4 spatial scales (entire catchment, 30m buffer, headwater buffer and 600 m upstream from the site) showed that, on average, the average proportion of agriculture was greatest for the entire catchment and smallest for the 600m buffer upstream from the site (Table 4.3). Differences among spatial scales for the average proportion of urban land followed the same pattern (Table 4.3). All urban descriptors were more variable than all agriculture descriptors for the rivers studied. Proportion urban 600m upstream from the site had the greatest variation whereas agriculture in the catchment had the smallest variation (Table 4.3). Overall, the proportion of urban activity in the catchment ranged from 0 through 28%, and the proportion of agriculture in the catchment ranged from 61% through 92% in the 29 rivers included in the study. STP descriptors demonstrated greater variability than urban and agriculture descriptors. Among the STP metrics total effluent discharge (m^3), STP population served per km^2, and distance upstream to the nearest STP (m) each demonstrated high variability. Of the STP descriptors total effluent discharge demonstrated the greatest variability (CV=2.0) among STP descriptors followed by STP population served per km^2 (CV=1.645).

Table 4.3. Descriptive statistics for land use descriptors measured in 29 catchments in southwestern Ontario. Urban and agriculture land use (proportion) was described at 4 spatial scales; catchment (C), buffer (buf), headwaters (HW) and 600m upstream from the site (600m). STP was described by 3 metrics; Total effluent discharged (STP - EFFQ) between May through November (m^3), population served by STP per km^2 (STP - persons), and distance from site to the nearest upstream STP (STP - distance). See Appendix E for training data.

Variables	Median	Mean	SD	CV	Min	Max
Urban-C	0.021	0.044	0.056	1.264	0.005	0.275
Ag-C	0.859	0.832	0.081	0.097	0.609	0.919
Urban-buf	0.02	0.04	0.045	1.127	0.007	0.21
Ag-buf	0.768	0.751	0.108	0.144	0.416	0.907
UrbanHW	0.016	0.035	0.044	1.262	0.004	0.224
AgHW	0.814	0.791	0.09	0.113	0.528	0.914
Urban600m	0.042	0.119	0.173	1.45	0	0.667
Ag600m	0.333	0.341	0.284	0.833	0	0.957
STP-EFFQ (m^3)	139,210	715,357	1,369,073	2	0	5,361,543
STP-persons	14.15	35.33	58.12	1.65	0	266.80
STP-distance	5935	19,378	25,430	1.31	0	94,235

Analysis of collinearity using VIF scores indicated significant collinearity between the proportion of urban activity in the catchment and proportion of urban activity in the 30m stream buffer (r=0.965; VIF=14.5). Likewise, collinearity was identified between the proportion urban activity in the catchment and urban activity in the headwaters (r=0.95; VIF=10.3)(Table 4.4). The proportion of urban in the catchment stream buffer and the proportion of urban activity in the headwater stream buffer were also significantly related (r=0.97; VIF=16.9). Urban activity 600m upstream from the site was not related to any of the other urban land use descriptors (VIF<1.4). Thus urban activity in the catchment stream buffer and urban in the headwaters were removed from further analyses. For agricultural land use descriptors we identified significant collinearity between the proportion agriculture in the catchment and proportion of agriculture in the 30m stream buffer (r=0.904; VIF=5.5). Significant collinearity was also identified between the proportion of agriculture in the catchment and agriculture in the headwaters (r=0924; VIF=6.8). Furthermore, proportion of agriculture in the stream buffer was significantly related to proportion of agriculture in the headwaters (r = 097; VIF = 16.9). Similar to urban activity, agriculture 600m upstream from the site was not significantly related to any of the land use descriptors (VIF<1.5). Based on the rule of an observed VIF greater than 5 the proportions of agriculture at the catchment stream buffers and headwater stream buffers were excluded from further analyses (Table 4). Significant collinearity was also identified between effluent discharge and STP population served per km^2 (r = 0.882; VIF = 7.7). Effluent discharge also demonstrated a slightly stronger association with distance (r = -0.756; VIF = 2.2) than the association between distance and STP population served per km2 (r = -0.7; VIF = 2.2) resulting in the removal of effluent discharge from further analyses.

Table 4.4 Results of an analysis of co-linearity among land use descriptors using Pearson Correlation analysis to calculate the variance inflationary factor (VIF). Significant associations (VIF > 5) are bolded. Arcsine transformation was applied to urban and agriculture descriptors; whereas, log(n+1) transformation was applied to STP metrics.

LU descriptor	URB-C	AG-C	Urb-buf	Ag-buf	UrbHW	AgHW	URB600m	AG600m	EFFQ	STP	Distance
URB-C	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
AG-C	-0.75 (2.3)	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Urb-buf	**0.97 (14.5)**	-0.68 (1.9)	-----	-----	-----	-----	-----	-----	-----	-----	-----
Ag-buf	-0.56 (1.5)	**0.90 (5.5)**	-0.50 (1.3)	-----	-----	-----	-----	-----	-----	-----	-----
UrbHW	**0.95 (10.3)**	-0.61 (1.6)	**0.97 (16.9)**	-0.41 (1.2)	-----	-----	-----	-----	-----	-----	-----
AgHW	-0.62 (1.6)	**0.92 (6.8)**	-0.56 (1.4)	**0.96 (11.9)**	-0.49 (1.3)	-----	-----	-----	-----	-----	-----
URB600m	0.35 (1.1)	0.35 (1.0)	0.34 (1.1)	0.05 (1.0)	0.36 (1.1)	-0.043 (1.0)	-----	-----	-----	-----	-----
AG600m	-0.43 (1.2)	-0.47 (1.3)	-0.33 (1.1)	0.54 (1.4)	-0.3 (1.1)	0.47 (1.3)	-0.14 (1.0)	-----	-----	-----	-----
EFFQ	0.54 (1.4)	-0.23 (1.1)	0.52 (1.4)	-0.19 (1.1)	0.46 (1.3)	-0.14 (1.1)	0.21 (1.0)	-0.31 (1.1)	-----	-----	-----
STP	0.6 (1.6)	-0.41 (1.2)	0.61 (1.6)	-0.36 (1.1)	0.52 (1.4)	-0.32 (1.1)	0.22 (1.0)	-0.30 (1.1)	**0.88 (7.7)**	-----	-----
Distance	-0.46 (1.3)	0.25 (1.1)	-0.49 (1.3)	0.17 (1.0)	-0.41 (1.2)	0.14 (1.0)	-0.17 (1.0)	0.21 (1.0)	-0.76 (2.2)	-0.7 (2.2)	-----

4.4 OLS Regression Models

Of the seven parameters modelled, OLS regression analysis identified significant relationships for all nutrient parameters except TDP. The NH_3 model was the only nutrient parameter modelled to have a negative coefficient for proportion agriculture in the catchment. For each model the initial parametric coefficients of significant variables were compared to bootstrapped coefficient estimates and indicated little to no deviation for all significant variables identified in the nutrient models.

The nutrient model for NH_3 demonstrated the strongest relationship among all nutrient parameters studied ($r^2 = 0.693$; $p < 0.0001$; $n = 25$) (Table 4.5). Average NH_3 concentrations were negatively associated with the proportion agriculture in the catchment and positively associated with STP population served per km^2. TKN was significantly associated with Ag-600m and STP population served per km^2. Ag-600m and STP population served per km^2 explained 36% of variation in TKN concentrations for the 29 rivers studied. TKN tended to increase almost 30% faster per unit increase in STP population served per km^2 compared to unit increases in Ag-600m (Table 4.5). Average NO_{3-}+NO_{2-} concentrations were associated with the proportion of urban and agricultural activity in the catchment. NO_{3-}+NO_{2-} concentrations tended to increase almost 25% faster per unit increase in proportion urban in the catchment compared to unit increases in proportion of agriculture in the catchment (Table 4.5). TN demonstrated the weakest relationship with land use among nutrient parameters. STP population served per km^2 in the catchment was the only significant predictor and explained 25% of the variation in TN (Table 4.5). SRP was associated with the same land use predictors as TKN (i.e., Ag-600m and STP). Together Ag-600m and STP population served per km^2 explained 30% of the variation in SRP among the 29 rivers. SRP tended to increase almost 40% faster per unit increase in STP population served per km^2 compared to unit increases in Ag-600m. (Table 4.5). TP was associated with the same predictor as TN (i.e., STP population served per km^2). However, STP population served per km^2 explained 36.3% of the variation in TP among the 29 rivers studied (Table 4.5).

Table 4.5. Results of Ordinary Least Squares regression analyses (OLS) relating average May-November nutrient concentrations to land use predictors for 29 southwestern Ontario catchments. Outliers are identified by site number in order of exclusion.

Modelled Parameter	R^2	Signif. F	Predictor Variables	Std. Coeff	p-value	Outliers	lower bound	upper bound
NH_3^-	0.693	0.0000	Agriculture catchment	-0.585	0.0001	41,2,38,13	-0.067	-0.024
			STP 2011 (pop./km2)	0.433	0.0022		0.002	0.007
TKN	0.362	0.0029	Agriculture 600m	0.37	0.0330	none	0.012	0.086
			STP 2011 (pop./km2)	0.598	0.0012		0.019	0.059
$NO_3^- + NO_2^-$	0.353	0.0043	Urban catchment	0.795	0.0011	18	0.448	2.316
			Agriculture catchment	0.527	0.0218		-0.279	1.872
TN	0.249	0.0080	STP 2011 (pop./km2)	0.499	0.0080	33,30	0.009	0.123
SRP	0.297	0.0122	Agriculture 600m	0.355	0.0539	1	0	0.022
			STP 2011 (pop./km2)	0.531	0.0057		0.003	0.013
TDP	----	----	----	----	> 0.1	----	----	----
TP	0.363	0.0005	STP 2011 (pop./km2)	0.602	0.0005	none	0.007	0.022

4.5 Model Performance and Evaluation

Evaluation of the performance of NO_{3-} +NO_{2-}, TN, SRP and TP nutrient models using the 3 types of model evaluation measures revealed that model performance varied between nitrogen and phosphorus forms in the data quality, spatial bounds, dry, moderate and wet year scenarios. Based on measures of overall model performance (i.e., disagreement measures and the average of the ratio of the averaged observed and expected concentrations) nitrogen models exhibited stronger performance than phosphorus models for all scenarios (Figure 2). Furthermore, NO_3-+NO_2- and TN models had substantially higher rates (43% through 79%) of success in predicting nutrient concentrations for individual evaluation sites than did SRP and TP models (10% through 38%).

4.5.1 NO_3-+NO_2- Model Evaluation

4.5.1.1 Disagreement measures

Disagreement measures used in the evaluation of NO_3^-+NO_2^- model performance identified that the data quality and moderate year scenarios had the lowest overall error between observed and expected concentrations among the five scenarios (Table 4.6). Although model evaluation resulted in no distinguishable difference in MAD values for the data quality and moderate year scenarios, the MAD was slightly greater for the data quality scenario. MSE and RMSE values indicated that NO_3^-+NO_2^- model performance was similar under the spatial scenario compared to the data quality scenario. However, MAD in the spatial scenario was greater than MAD in the data quality and moderate scenarios indicating that there was a higher magnitude of error at sites evaluated in the spatial scenario. Examination of observed and expected concentrations revealed that 11-Black Creek, 25-McGregor Creek and 35-Penetangore River were the main sources of error in the spatial scenario. In contrast, the data quality and moderate scenarios had lower magnitude of errors between observed and expected concentrations and greater dispersion of error among evaluation sites (Figure 4.3). RMSE was greatest under the dry and wet scenarios, indicating the weakest model performance among the five scenarios (Table 4.6). MSE was slightly greater in the dry year compared to the wet year scenario suggesting a larger difference between observed and expected concentrations for evaluation sites in the dry year (Table 4.6). Examination of observed and expected concentrations from evaluation sites revealed that the dry year had 6 sites acting as large sources of error (>1sd); whereas, the wet year had 5 sites with large error among the 14 evaluation sites. 12-Boyle Drain, 15-Conostogo Creek, 1-Little Ausable River, 19-Moorehead Creek, 30-Nanticoke Creek and the 33-North (Upper) Thames River were the main sources of error for the dry scenario; whereas 6-Beachamps Drain, 15-Conostogo

Creek, 28-Middle Thames River, 30-Nanticoke Creek and the 33-North (Upper) Thames River were the main source of model error for the wet scenario (Figure 4.3).

Comparison of the average of the May through November observed NO_3^-+NO_2^- concentrations (Ō) to average of the May through November expected NO_3^-+NO_2^- concentrations (Ē) revealed that the NO_3^-+NO_2^- model performed best under the data quality scenario, predicting the average expected NO_3^-+NO_2^- concentration within 1% of the average of the observed concentration (Table 4.6). However, the standard deviation (*SD*=2.20) suggested that observed NO_3^-+NO_2^- concentrations ranged well beyond the mean (Ō = 4.12mg/L) and had greater variability compared to the expected NO_3^-+NO_2^- concentrations (Table 4.6). Examination of observed and expected concentrations from evaluation sites identified random dispersion of NO_3^-+NO_2^- concentrations in the data quality scenario (Figure 4.3). Evaluation of NO_3^-+NO_2^- model performance using average of the May through November observed (Ō) and expected (Ē) concentrations revealed that the model tended to over predict NO_3^-+NO_2^- concentration by 40% in the spatial scenario and 10% in the dry year scenario, respectively. The 40% over prediction for the spatial scenario was the poorest performance of the model under any of the five scenarios. Observed values in the spatial scenario had the lowest Ō and standard deviation among all scenarios (Table 4.6). In contrast, the standard deviation of the Ō was greatest under the dry year scenario (Table 4.6). Examination of observed concentrations from the 14 evaluation sites revealed the greatest variability and dispersion of concentrations in the dry year scenario (Figure 5). Evaluation of NO_3^-+NO_2^- model performance in the moderate and wet year scenarios revealed that the model had a tendency to under predict the average of the observed compared to the average of the expected by 12% in the moderate scenario and 22% in the wet scenario, respectively (Table 4.6). Standard deviation in the wet year exhibited greater dispersion of observed values within the 14 evaluation sites than for the moderate year scenario.

4.5.1.2 Agreement measures

The Nash Sutcliffe Efficiency Index (Ef) revealed that the NO_3^-+NO_2^- model predicted as successfully as the mean of the observed data under almost all scenarios (Ef

$\leq$ 0), with the exception of the data quality scenario where the model predicted slightly better than the mean of the observed data (Ef=0.25). Results for individual site O:E scores were similar and revealed that the NO_3^-+NO_2^- model successfully predicted NO_3^- + NO_2^- concentrations for the majority of sites where the observed value did not deviate more than 1 standard deviation from the mean of the training data (Figure 4.3). Site O:E scores indicated acceptable predictions (0.80≥O:E≤ 1.20) were found under all scenarios for sites located on the 2-Avon River, 13-Canagagigue Creek, 22-Kettle Creek, 24-Lynn River, 32-Upper Nith River, and 39-South Maitland River (Table 4.7). Contrary to the 1% difference between the percent overall $\bar{O}$ compared to $\bar{E}$, O:E scores under the data quality scenario suggested modest prediction performance with only 54% of the evaluation sites being successfully predicted by the NO_3^-+NO_2^- model (Table 4.6). In contrast, under the spatial scenario the NO_3^-+NO_2^- model successfully predicted 70% of NO_3^-+NO_2^- concentrations at the 10 evaluation sites (Table 4.6). Among the 10 evaluation sites included in the spatial scenario, 11-Black Creek, 25-McGregor Creek and 35-Penetangore River sites were identified to be strongly over predicted (Table 4.7). The NO_3^-+NO_2^- model was least successful in predicting in-stream concentrations under the dry year scenario, successfully predicting only 43% of the 14 streams evaluated (Table 4.6). Furthermore, the mean and median of O:E scores were low in the dry year scenario indicating that the model frequently over predicted concentrations (Table 4.6). The NO_3^-+NO_2^- model performed best under the moderate year scenario with successful prediction of mean NO_3^-+NO_2^- concentrations at 79% of the evaluation streams (Table 4.6). However, under the moderate year scenario the model did have difficulty predicting concentrations at 6-Beauchamps Creek, 28-Middle Thames River and 30-Nanticoke Creek where the observed May through November averages were beyond 1 standard deviation from the mean of the training data (Figure 4.3-D or Table 4.7). Last, site O:E scores for the wet year scenario revealed that the model tended to under predict NO_3^-+NO_2^- concentrations at the 14 evaluation sites and only successfully predicted concentrations 50% of the time (Table 4.6).

Table 4.6: Model performance under five scenarios (data quality, spatial bounds, dry, moderate and wet years) for NO3-+NO2-, TN, SRP and TP models based on measures of disagreement (MAD, MSE, RMSE) and measures of agreement (O:E) at both the overall model level and individual evaluation site.

Nutrient Parameter	Year	n	Disagreement Measures (mg/L) MAD	MSE	RMSE	Average of the Averaged (mg/L) Ō (SD)	Ē (SD)	% Diff.	NSE	Site O:E Scores Mean	Median	Min	Max	% Success
NO_{3^-} +NO_{2^-}	Data Quality	13	0.74	3.36	1.83	4.12 (2.20)	4.06 (1.24)	1	0.25	0.98	0.91	0.68	1.36	54
	Spatial	10	1.14	3.26	1.81	2.78 (0.99)	3.89 (1.07)	40	-1.76	0.84	0.92	0.43	1.08	70
	Dry	14	1.08	8.54	2.92	3.61 (3.28)	3.98 (0.87)	10	-0.02	0.85	0.82	0.35	1.51	43
	Moderate	14	0.78	2.81	1.68	4.54 (1.54)	3.98 (0.87)	12	-0.18	1.06	1.06	0.56	1.44	79
	Wet	14	1.34	8.00	2.83	5.11 (2.73)	3.98 (0.87)	22	-0.09	1.08	1.12	0.61	1.51	50
TN	Data Quality	13	1.39	6.19	2.49	4.74 (2.60)	4.77 (0.73)	0.01	-0.11	0.95	1.00	0.32	1.40	77
	Spatial	10	0.56	1.26	1.12	3.68 (1.03)	4.43 (0.61)	20	-0.29	0.90	0.92	0.66	1.10	70
	Dry	14	1.40	9.88	3.14	4.27 (3.37)	4.58 (0.65)	7	-0.08	0.89	0.84	0.50	1.54	50
	Moderate	14	0.97	3.70	1.92	5.41 (1.61)	4.58 (0.65)	15	-0.44	1.07	1.09	0.63	1.32	71
	Wet	14	1.38	9.14	3.02	6.01 (2.66)	4.60 (0.66)	23	-0.51	1.11	1.12	0.74	1.55	71
SRP	Data Quality	13	0.0092	0.00042	0.020	0.030 (0.024)	0.036 (0.016)	20	0.23	0.74	0.62	0.22	1.77	38
	Spatial	10	0.046	0.0065	0.081	0.054 (0.083)	0.023 (0.016)	57	-0.04	2.31	1.28	0.34	8.29	10
	Dry	14	0.022	0.0017	0.041	0.045 (0.050)	0.033 (0.015)	26	0.31	1.14	0.96	0.29	3.20	29
	Moderate	14	0.0092	0.00049	0.022	0.042 (0.024)	0.033 (0.015)	21	0.05	1.50	1.31	0.25	3.66	14
	Wet	14	0.013	0.00071	0.027	0.034 (0.034)	0.033 (0.015)	3	0.36	0.93	0.78	0.29	2.47	21
TP	Data Quality	13	0.016	0.0015	0.038	0.079 (0.052)	0.086 (0.030)	9	0.41	0.89	0.74	0.33	1.76	31
	Spatial	10	0.054	0.012	0.110	0.11 (0.114)	0.072 (0.026)	22	-0.02	1.45	1.05	0.33	4.17	30
	Dry	14	0.030	0.0032	0.057	0.098 (0.071)	0.078 (0.027)	20	0.34	1.15	1.09	0.41	2.08	14
	Moderate	13	0.018	0.0013	0.036	0.087 (0.036)	0.078 (0.027)	10	0.43	1.11	1.17	0.37	1.67	38
	Wet	14	0.027	0.0030	0.055	0.095 (0.073)	0.079 (0.028)	17	0.41	1.08	1.04	0.40	2.37	29

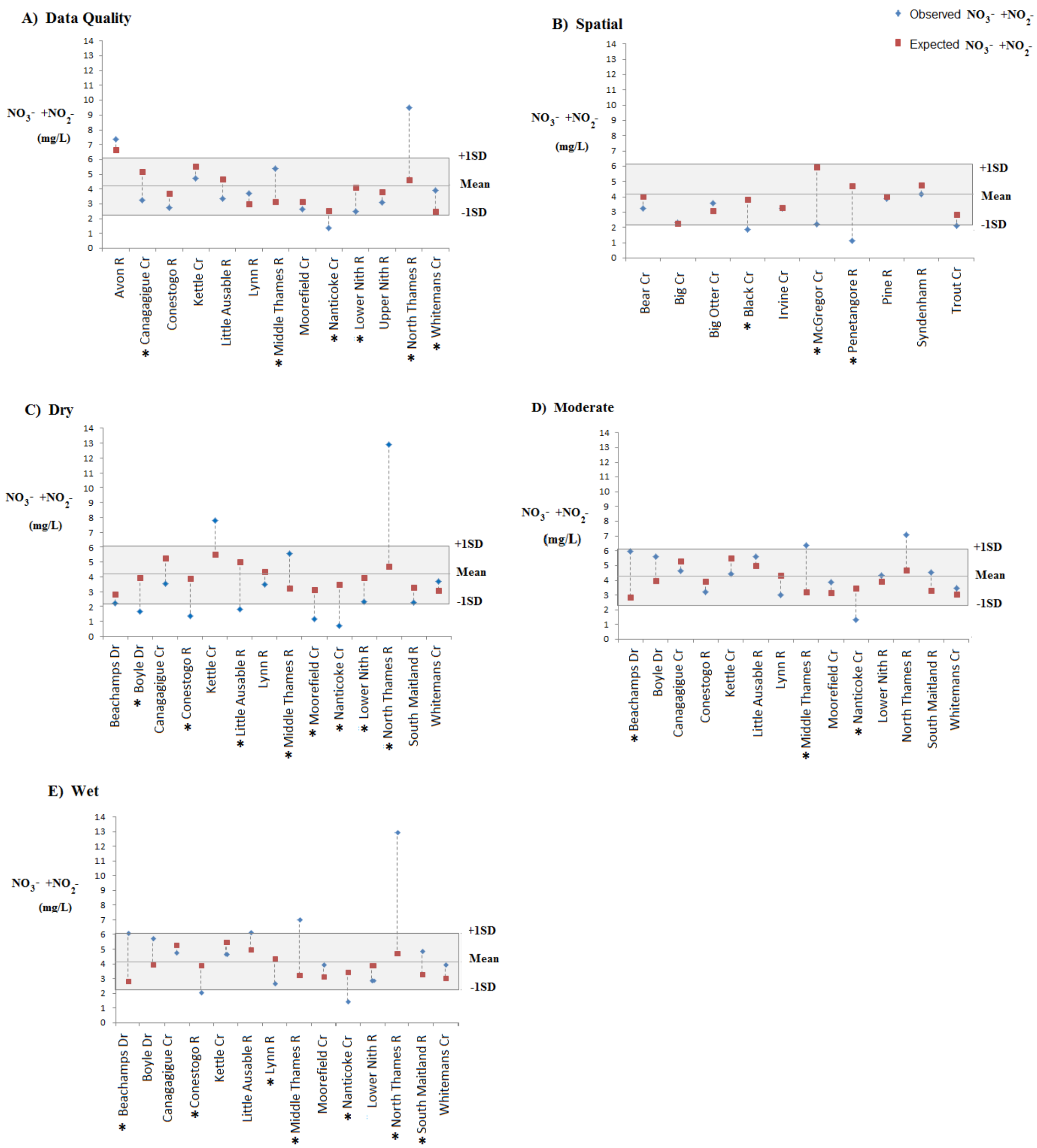

Figure 4.3. The Observed vs. Expected NO_3^-+NO_2^- and TN values calculated to evaluate model performance at individual sites in five scenarios; A) data quality, B) spatial, C) dry, D) moderate and E) wet year scenarios. Sites exceeding the O:E accepted accuracy measure are marked with an asterisk (*).

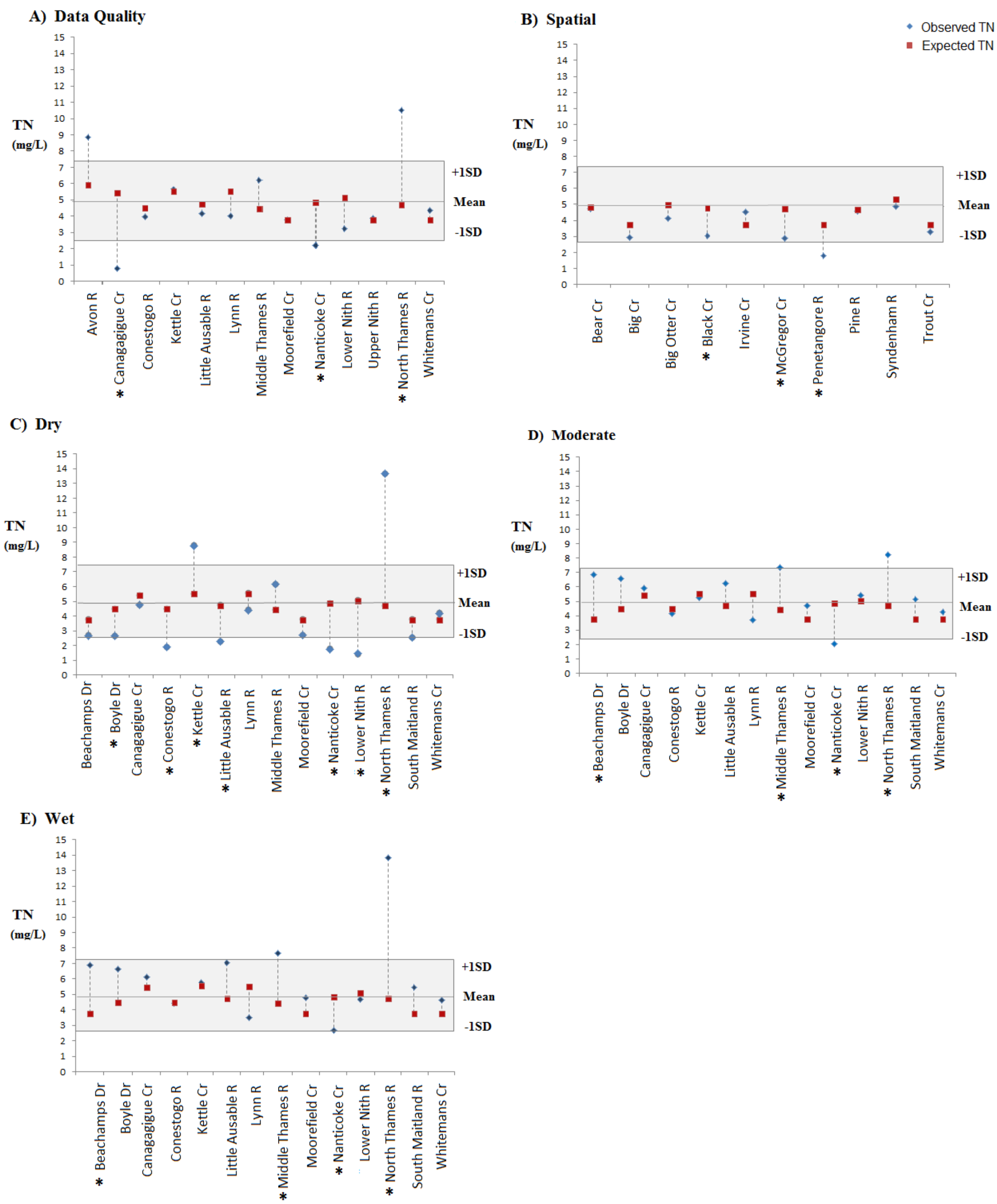

Figure 4.4. The Observed vs. Expected TN values calculated to evaluate model performance at individual sites in five scenarios; A) data quality, B) spatial, C) dry, D) moderate and E) wet year scenarios. Sites exceeding the O:E accepted accuracy measure are marked with an asterisk (*).

4.5.2 TN Model Evaluation

4.5.2.1 Disagreement measures

Evaluation of TN model performance using disagreement measures identified that the spatial scenario exhibited the lowest error between observed and expected concentrations among the five scenarios (Table 6). Among the 10 evaluation sites, Black Creek, McGregor Creek and Penetangore River were identified as the main sources of error in the spatial scenario (Figure 4.4-B). The MAD in the data quality scenario was 2 times larger than the MAD in the spatial scenario which combined with the greater MSE value suggested substantially larger magnitude of error compared to the spatial scenario (Table 4.6). Examination of individual sites indicated the main source of the error in the data quality scenario was from over prediction of the TN concentrations at Canagagigue and Nanticoke Creeks as well as under prediction at the North Thames River site (Figure 4.4-A of Table 4.7). MAD and RMSE disagreement measures for the moderate year were almost twice that of the spatial scenario (Table 4.6). Examination of individual sites identified error under the moderate year scenario to be evenly distributed among the 14 evaluation sites (Figure 4.4-D of Table 4.7). In contrast, the dry and wet year scenarios had the highest magnitude of error between observed and expected TN concentrations among the 3 climate scenarios, with the RMSE largest in the dry scenario (Table 4.6). Although MAD resulted in no distinguishable difference in model performance between dry and wet scenarios examination of MSE values identified a greater magnitude of error in the dry year. Examination of sites identified 7 evaluation sites (i.e., 12-Boyle Creek, 15-Conestogo Creek, 22-Kettle Creek,23- Little Ausable River, 30-Nanticoke Creek, the 31-Lower Nith River and the 33-North (Upper) Thames River) with large error in the dry year scenario compared to only 4 sites (i.e., 6-Beachamps Drain, 28-Middle Thames River, 30-Nanticoke Creek and the 33-North (Upper) Thames River) exhibiting large error in the wet year (Figure 4.4-E or Table 4.7).

Evaluation of TN model performance using the average of the May through November concentrations revealed less than 1% difference between $\bar{O}$ compared to $\bar{E}$ for the data quality scenario (Table 6). However, the standard deviation for the observed concentrations (SD=2.6) was more than double that of the expected (SD=0.73).

Examination of evaluation sites in the data quality scenario identified random distribution of error, with the largest observed TN concentration almost double that of the mean of the training data in the 33-North (Upper) Thames River (Figure 4.4-A). In contrast, the TN model exhibited the poorest performance under the spatial scenario and wet year scenarios where the differences between Ē and Ō concentrations were about 20% (Table 4.6). However, dispersion among the 10 evaluation sites was lowest (SD=1.03) for the spatial scenario. The Ō concentration was largest for the wet year scenario with a standard deviation of almost 4 times that of the Ē concentrations suggesting extreme TN concentrations were captured in this scenario. Examination of individual sites in the wet climate scenario identified that the 33-North (Upper) Thames River had an Ō that was almost 3 times the mean of the training data (Figure 4.4-E or Table 4.7). Ō:Ē also identified that the TN concentration was only over predicted by 7% for the dry year scenario yet observed concentrations in the dry scenario had the largest standard deviation among all scenarios (SD=3.37) (Table 4.6). Comparison of TN Ō to Ē concentrations revealed that the TN model tended to under predict concentration by 15% in the moderate year scenario. Standard deviation for the moderate scenario (SD=1.61) was less than the standard deviation for the data quality, dry and wet scenarios (SD≥2.6) indicating lower dispersion in the moderate compared to the other climate and quality scenarios.

4.5.2.2 Agreement measures

The predictive power of the TN model was found to be only as good as the mean of the observed data under all scenarios as revealed by the Nash Sutcliffe Efficiency Index. The efficiency index results are contrary to the site O:E scores that identified the TN model to have the strongest performance of the 4 models evaluated. Evaluation of TN model performance using the Site O:E scores revealed that the model successfully predicted 77% of evaluation sites in the data quality scenario. However, the data quality scenario exhibited the largest range of Site O:E scores (0.32 to 1.40) indicating that evaluation sites were highly dispersed. Examination of evaluation sites that were not successfully predicted in the data quality scenario revealed that observed concentrations deviated more than 1 standard deviation from the mean of the training data for the 13-Canagagigue Creek, 30-Nanticoke Creek and the 33-North (Upper) Thames River (Figure

4.4 of Table 4.7). TN model performance consistently predicted ≥70% of evaluation sites under the spatial, moderate and wet year scenarios. However, examination of individual sites in the wet and moderate scenarios revealed that 6-Beauchamps Drain, 28-Middle Thames River, 30-Nanticoke Creek and the 33-North (Upper) Thames River were consistently under predicted (Figure 4.4-E or Table 4.7). Contrary to the 7 % difference between overall Ō and Ē concentrations, site O:E scores indicated that the model exhibited the poorest performance in the dry year scenario, successfully predicting only 50% of evaluation sites (Table 4.6).

4.5.3 SRP Model Evaluation

4.5.3.1 Disagreement measures

Evaluation of SRP model performance using disagreement measures identified the lowest magnitude of error between observed and expected SRP concentrations in the data quality and moderate year scenario (Table 4.6). MAD and MSE were slightly greater in the wet year scenario compared to the data quality and moderate year scenarios suggesting larger difference between observed and expected SRP concentration at individual sites for the wet year scenario (Table 4.6). Examination of individual sites identified a larger magnitude of error for Kettle Creek in the wet scenario compared to the data quality and moderate scenarios (Figure 4.5 or Table 4.7). The largest magnitude of error between observed and expected concentrations was identified in the spatial scenario (MAD=0.046; MSE=0.0065). RMSE indicated that SRP model performance was weakest outside of the spatial bounds of the derived SRP model (Table 4.6). Examination of individual sites revealed that 9 out of the 10 evaluation sites had large differences between observed and expected SRP concentrations (Table 4.7).

Comparison of the average of the May through November observed to expected concentration identified that expected concentrations were predicted with ≥20% inaccuracy for all scenarios with the exception of the wet year scenario (3%) (Table 4.6). Contrary to RMSE which identified the strongest model performance for the data quality and moderate scenarios, the overall Ō:Ē revealed that the model over predicted SRP concentration by 20% in the data quality scenario and by 21% in the moderate scenario

(Table 4.6). Both data quality and moderate scenarios exhibited the lowest variability (*SD*=0.024) among the five scenarios. Model performance was weakest for the spatial scenario and under predicted the Ō concentration by 57% (Table 4.6). Examination of evaluation sites identified particularly large differences between observed and expected concentrations for 5-Bear Creek and 25-McGregor Creek (Figure 4.5-B of Table 4.7). The observed concentration for 25-McGregor Creek was identified to be 7 times larger than the expected concentration and almost 3 times larger than the expected concentration at 5-Bear Creek. The large observed concentrations at both of these sites was likely responsible for the large difference between Ō and Ē concentrations. Comparison of overall Ē to Ō identified that the model under predicted SRP concentration by 26% under the dry scenario (Table 4.6). Observed concentration at 22-Kettle Creek and the 33-North (Upper) Thames River were identified to be almost 4 times larger than the expected concentration, having a large effect on the Ō in the dry scenario. The overall Ō to Ē revealed that SRP model performance was strongest in the wet year scenario where the model under predicted concentration by 3%.

4.5.3.2 Agreement measures

Contrary to disagreement measures, the Nash Sutcliffe Efficiency Index revealed relatively strong predictive power for the SRP model compared to the prediction power of the nitrogen models. The efficiency index was greater than 0 for 4 of the 5 scenarios indicating the model predicted better than the mean of the observed data. Results from analysis of the evaluation site O:E scores, however, revealed that the SRP model consistently did not predict stream SRP concentrations in evaluation streams. Evaluation of individual site performance found that the SRP model tended to successfully predict SRP concentrations at less than 40% of the evaluation sites for all five scenarios, which is the lowest prediction power among the models evaluated (Table 4.6). The model had the strongest performance in the data quality scenario, successfully predicting 38% of evaluation sites. SRP concentrations were successfully predicted in the dry year (29%) and wet year (21%) scenarios at 29% and 21% of evaluation sites, respectively. Examination of evaluation sites revealed that the majority of concentrations were within 1 standard deviation of the training data's mean. However, the differences between observed and expected values were dispersed among sites in each scenario and revealed no trend in phosphorus concentrations at individual evaluation sites (Table 4.7). SRP model performance was weakest under the spatial and moderate year scenarios, successfully predicting only 10% and 14% of evaluation sites, respectively (Table 4.6). Mean and median site O:E scores in the spatial (Mean=2.31; Median=1.28) and moderate (Mean=1.50; Median=1.31) scenarios indicated that the model tended to under predict SRP concentration (Table 4.6). Examination of evaluation sites revealed that 5-Bear Creek, 11-Black Creek, 20-Irvine Creek and 25-McGregor Creek were all under predicted in the spatial scenario; whereas, 6-Beauchamps Drain, 12-Boyle Drain, 13-13-Canagagigue Creek, 21-Kettle Creek, 24-Lynn River, 27-Middle Thames River, 39-South Maitland River and 49-Whitemans Creek were all under predicted in the moderate scenario (Figure 4.5-D of Table 4.7). Furthermore, the observed concentration for 25-McGregor Creek was identified to be 7 times larger than the expected concentration and almost 3 times larger than the expected concentration at 5-Bear Creek, consistent with differences identified between Ē and Ō.

4.5.4 TP Model Evaluation

4.5.4.1 Disagreement measures

Similar to SRP model performance, disagreement measures revealed that the TP model performance was strongest in the data quality and moderate scenarios and RMSE revealed that the model performed best in the moderate scenario (RMSE=0.036) (Table 4.6). In contrast, the spatial scenario had the highest magnitude of error between observed and expected TP concentrations (Table 4.6). The MSE was also largest in the spatial scenario (Table 4.6). Examination of individual sites revealed that the observed TP concentration (0.49 mg/L) at McGregor Creek was almost 9 times the expected concentration (0.086 mg/L) and were the highest concentrations of evaluation sites in all scenarios. MAD and MSE identified that the error between observed and expected concentrations was similar in the dry and wet year scenarios. Likewise, no distinguishable difference in RMSE was detected between the dry and wet scenarios (Table 4.6). Examination of individual sites TP concentrations identified large difference between observed and expected values at 12 of the 14 sites in the dry scenario and 9 of the 14 sites in the wet scenario (Figure 4.6 of Table 4.7).

Table 4.7. Site O:E scores for evaluation sites under five scenarios; data quality, spatial bounds, dry, moderate and wet years. Successful prediction of nutrients concentrations at individual sites are highlighted in green using ±0.20 error around the O:E=1.

Nutrient	Year	n	Avon R	Beauchamps Dr	Boyle Dr	Canagagigue Cr	Conestogo R	Kettle Cr	Little Ausable R	Lynn R	Middle Thames R	Moorefield Cr	Nanticoke Cr	Lower Nith R	Upper Nith R	North Thames R	South Maitland R	Whitemans Cr
NO_3^- +NO_2^-	Data Quality	13	1.04			0.79	0.85	0.93	0.85	1.11	1.31	0.91	0.68	0.77	0.90	1.36		1.27
	Dry	14		0.86	0.61	0.83	0.54	1.16	0.58	0.89	1.30	0.55	0.35	0.75		1.51	0.81	1.10
	Moderate	14		1.44	1.18	0.94	0.90	0.91	1.06	0.83	1.38	1.11	0.56	1.05		1.20	1.17	1.06
	Wet	14		1.46	1.20	0.96	0.71	0.93	1.10	0.78	1.44	1.13	0.61	0.86		1.51	1.22	1.15
TN	Data Quality	13	1.18			0.32	0.94	1.01	0.94	0.86	1.17	1.00	0.66	0.80	1.01	1.40		1.08
	Dry	14		0.83	0.76	0.94	0.62	1.22	0.68	0.90	1.16	0.84	0.57	0.50		1.54	0.81	1.06
	Moderate	14		1.32	1.19	1.04	0.96	0.98	1.14	0.83	1.25	1.12	0.63	1.03		1.28	1.16	1.06
	Wet	14		1.33	1.20	1.06	1.00	1.02	1.19	0.80	1.27	1.13	0.74	0.96		1.55	1.19	1.11
SRP	Data Quality	13	0.83			0.58	0.64	1.77	0.32	0.90	0.59	0.45	1.16	0.22	0.28	1.09		n/a
	Dry	14		0.99	0.29	1.42	0.99	2.61	0.36	0.83	0.42	0.33	0.92	1.57		3.20	0.63	1.37
	Moderate	14		1.41	1.84	1.33	1.28	1.26	0.25	2.16	1.53	1.14	0.44	0.92		0.69	3.05	3.66
	Wet	14		0.59	0.57	0.84	0.46	2.47	1.80	0.76	0.79	0.37	1.76	0.42		0.86	0.29	1.01
TP	Data Quality	13	0.99			0.74	0.86	1.76	0.52	0.59	0.70	1.60	1.17	0.61	0.54	1.14		0.33
	Dry	14		1.19	0.68	1.40	1.00	1.82	0.41	0.78	0.45	1.27	1.68	1.99		2.08	0.68	0.70
	Moderate	14		1.29	1.17	1.23	0.98	1.37	0.37	1.01	0.89	1.67	1.22			0.94	0.74	1.61
	Wet	14		0.82	0.54	1.40	0.58	1.95	1.22	0.92	0.58	1.16	2.37	1.16		1.39	0.40	0.67

Nutrient	Scenario	n	Bear Cr	Big Cr	Big Otter Cr	Black Cr	Irvine Cr	McGregor Cr	Penetangore R	Pine R	Sydenham R	Trout Cr
NO_3^- +NO_2^-	Spatial	10	0.90	1.01	1.08	0.67	0.99	0.60	0.43	0.98	0.94	0.84
TN	Spatial	10	0.99	0.88	0.91	0.79	1.10	0.78	0.66	0.99	0.96	0.93
SRP	Spatial	10	2.69	n/a	0.50	1.62	3.60	8.29	n/a	0.34	0.93	0.54
TP	Spatial	10	1.78	0.98	0.60	1.11	2.28	4.17	0.46	0.33	0.91	1.91

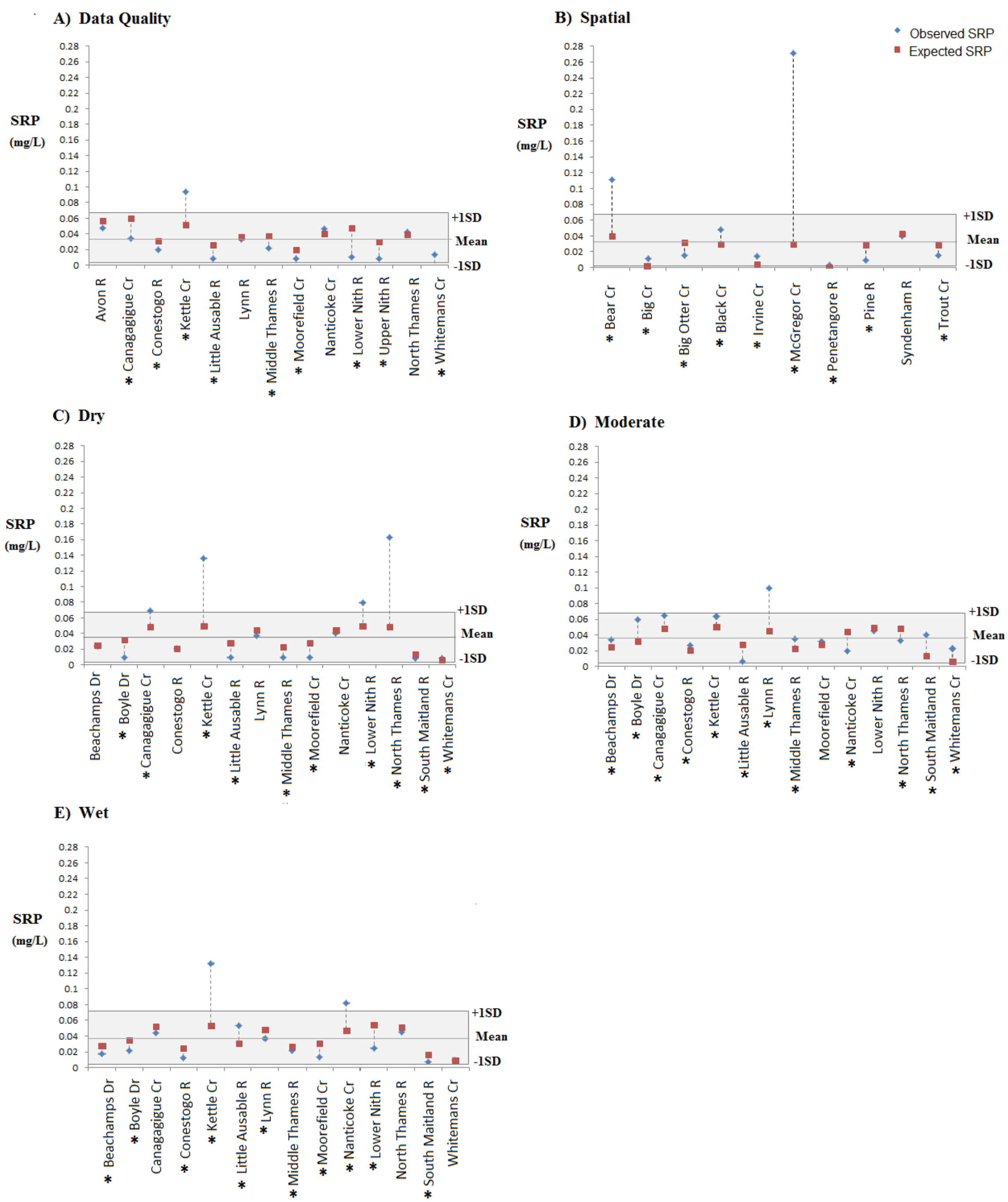

Figure 4.5. The Observed vs. Expected SRP concentrations were calculated to evaluate model performance at individual sites in five scenarios; A) data quality, B) spatial, C) dry, D) moderate and E) wet year scenarios. Sites exceeding the O:E accepted accuracy measure are marked with an asterisk (*).

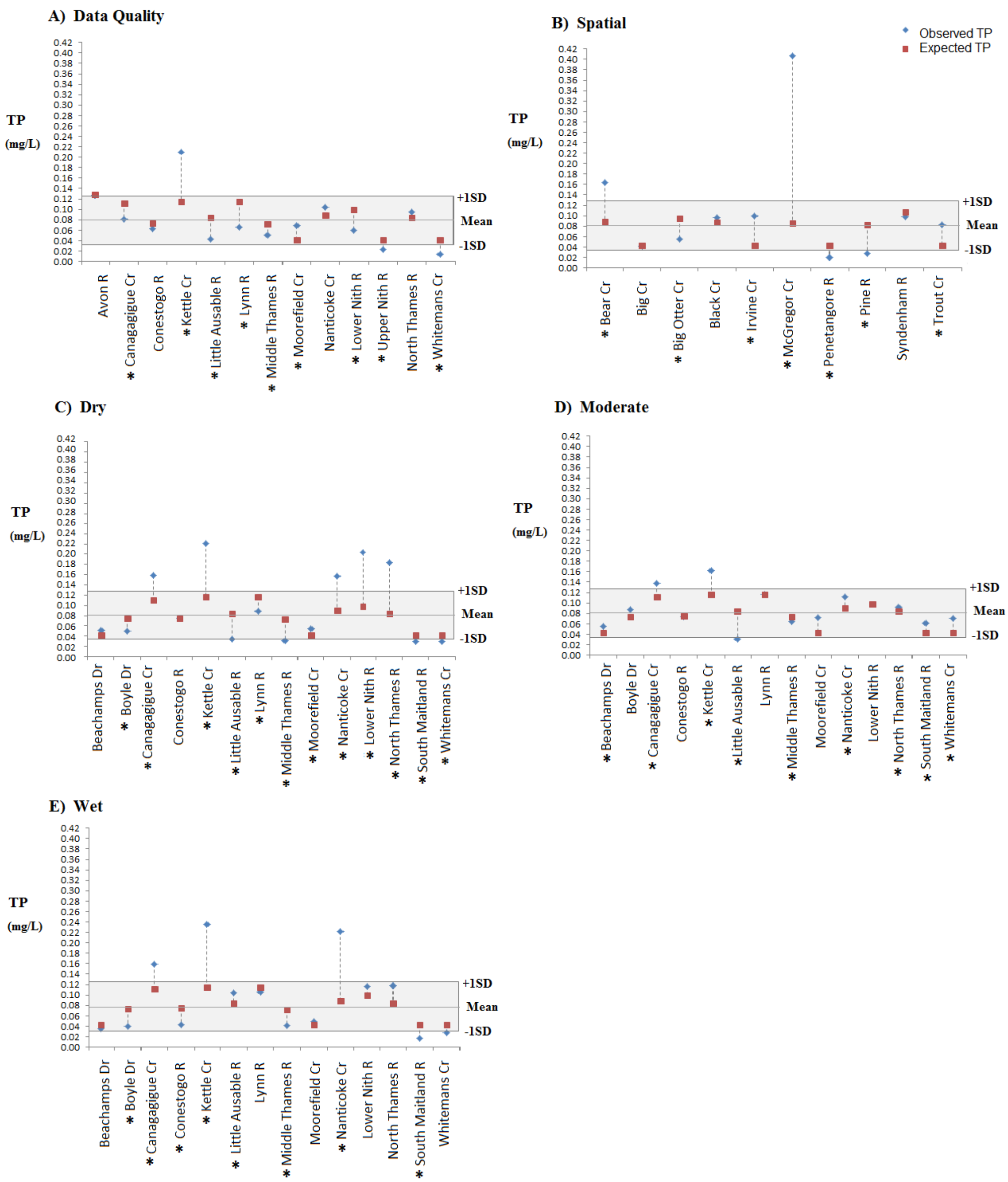

Figure 4.6. The Observed vs. Expected TP concentrations were calculated to evaluate model performance at individual sites in five scenarios; A) data quality, B) spatial, C) dry, D) moderate and E) wet year scenarios. Sites exceeding the O:E accepted accuracy measure are marked with an asterisk (*).

Comparison of $\bar{O}$ and $\bar{E}$ concentrations suggested that the TP model performed best under the data quality and moderate scenarios where TP concentrations were under-predicted by 9% and over-predicted 10%, respectively (Table 4.6). The error was more evenly dispersed among evaluation sites in the moderate scenario compared to the compared to the data quality scenario. Examination of evaluation sites in the data quality scenario identified the greatest error between the observed and expected concentration was in Kettle Creek (Figure 4.6). In the spatial scenario TP concentration was under predicted by 22% in large part due to large under predictions of TP concentrations at 5-Bear and 25-McGregor Creeks (Table 4.7 or Figure 4.6). The standard deviation of the $\bar{O}$ TP concentration was also largest under the spatial scenario indicating high dispersion of concentrations around the mean (Table 4.6). The TP model performance in the dry and wet scenarios was similar to the spatial scenario where concentrations were under predicted by 20% and 17%, respectively. Examination of evaluation sites revealed that the difference between observed and expected concentrations was random in both scenarios (Figure 4.6).

4.5.4.2 Agreement measures

The TP model results for model performance using the Nash Sutcliffe Efficiency Index revealed that the plot of the observed TP concentrations versus the expected concentrations was the closest fit to the 1:1 line compared to the other 3 nutrient models evaluated (NO_3^-+NO_2^-, TN and SRP). Dispersion among the observed and expected values, however, have been noted to influence the Ef resulting in overestimation of model performance. Results from Site O:E scores revealed that the TP model successfully predicted TP concentrations at <40% of the evaluation sites for all five scenarios (Table 4.6). TP model performance was best in the moderate scenario, however, only successfully predicted 38% of evaluation sites. Approximately 30% of evaluation sites were successfully predicted for the data quality, spatial and wet scenarios (Table 4.6). However, the mean site O:E score revealed that the model tended to under predict TP concentration in the spatial scenario and 3 climate scenarios whereas it over predicted under the data quality scenario (Table 4.6). Examination of evaluation sites revealed that the difference between observed and expected concentrations was randomly distributed among evaluation sites for each scenario (Figure 4.6 or Table 4.7). The model performance was weakest for the dry scenario where only 14% of evaluation sites were successfully predicted. Examination of evaluation sites identified successful prediction of TP concentration at 6-Beachamps Drain, 15-Conestogo Creek and 24-Lynn Creek (Figure 4.6 or Table 4.7).

5 Discussion

Concentrations of nitrogen and phosphorus in streams sampled for our study were similar to those found by past regional studies in temperate North America (Barton, 1997; Omernik, 1977; Sliva et al., 2001; Walker & Tossell, 1992). For example, the May through November 2012 mean nitrogen and phosphorus concentrations observed in our study streams (3.0 < TN= <8.5mg/L; 0.028 < TP <0.79 mg/L) were comparable to mean concentrations (TN >3.0mg/L, <8.5mg/L; TP= >0.028 mg/L, <0.79 mg/L) observed in agricultural catchments located in Ohio, Ontario, Quebec, Michigan and Missouri (Barton & Farmer, 1997; Chambers et al., 2012; Hill et al., 2011; Johnson et al., 1997; Sliva & Williams, 2001). Our TN and TP concentrations were particularly similar to summer stream TN and to a lesser extent TP concentrations measured by Johnson et al. (1997) for the Coastal basin (TN=4.78; TP=0.031) and Cass River (TN=4.13; TP=0.045) catchments of eastern Michigan perhaps because of the similar range of agricultural land cover (i.e., 45% - 98%). The more modest differences (TN= 46%; TP<25%) between our results and three Ontario based studies (i.e., Barton & Farmer, 1997; Chambers et al., 2010; Sliva & Williams, 2001) are likely attributable to differences in study objectives and associated site selections as well temporal differences in sample collection.

In a now dated, large-scale study of water chemistry in the conterminous United States of America Omernik (1977) recorded mean TN concentration of 4.17 mg/L and mean TP concentration 0.135 mg/L (N:P, 26:1) in streams of the eastern United States with >75% agriculture and <7% urban development. TN concentrations in our streams were consistent with the stream nutrient concentrations found by Omernik (1977) in the corn belt and dairy region. However, one notable difference between our findings and Omernik's is that our mean TP concentrations were on average 40% lower than

Omernik's. Since Omernik's regional study was conducted there have been changes to provincial and federal regulations regarding the quality and quantity of STP effluent that has resulted in the removal of nutrients from waste water, most notably phosphorus (GLWQA, 1978). Best management practices have also been widely adopted in urban and agricultural lands to improve stream water quality (Barton & Farmer, 1997; Chambers et al., 2012; Dolan et al., 2012; GLWQA, 1978; Tuppad et al., 2010). For example, BMP's implemented in agricultural catchments resulted in decreasing trends in organic nitrogen, SRP and TP in streams located in Texas (Tuppad et al., 2010). Likewise, Yates et al. (2006a) found that no-till practices were significantly associated with decreased suspended sediment and phosphorus concentrations in streams located in the Upper Thames River watershed in southern Ontario. These regulatory and landscape management actions likely account for much of the difference between our findings and those of Omernik’s from 40 years ago.

Stream nutrient concentrations observed in our study regularly exceeded Provincial Water Quality Objectives (PWQO) and Canadian Environmental Quality Guidelines (CEQG) of phosphorus for the protection of aquatic life. Of the 29 streams sampled, 26 streams exceed CEQG meso-eutrophic trigger range for mean TP (0.02 - 0.035 mg/L; CCME, 2004). Three of the seven sites that did not have an STP in their catchment were the only sites below the PWQO standard for TP (0.03 mg/L)(Ontario Ministry of Environment and Energy, 1994). These results suggest that STP effluent is linked to guideline exceedances of stream concentrations of TP. Furthermore, these results are consistent with past studies that have identified STP effluent as a point source that introduces excess phosphorus to the aquatic system through effluent containing by-products of human waste and detergents (Jarvie et al., 2006; Sanchez-Perez et al., 2009). In contrast, the mean May through November $NO_3^-+NO_2^-$ concentration did not exceed provincial or national objectives for nitrate (13.0mg/L) (CEQG, 2012) and nitrite (0.06mg/L) (PWQO, 2006). However, further examination of the 10 samples collected from each of the 29 streams sampled revealed that 16 of the 29 streams exhibited concentrations of $NO_3^-+NO_2^-$ during the June sample collection time that were >1.5 times the CEQG guideline of 13.0 mg/L (long-term exposure)(CEQG, 2012) (CWQG, 2012). Our June $NO_3^-+NO_2^-$ results are consistent with Johnson et al. (1997) who also measured the greatest concentration of NO_3^-+NO_2^- and TN during the summer period in streams with catchment land use dominated by row crop agriculture. Results from other previous studies suggest that the elevated concentration of nitrogen during the spring (May-June) in agricultural catchments may be linked to the application of fertilizers and manure on row crop agricultural fields (Kanwar et al., 2006). Our findings suggest that management strategies aimed at land use and wastewater treatment practices are needed to reduce stream nutrient concentrations in our study region to meet provincial and national recommendations.

Results from our study indicated that catchment vegetation condition, measured as NDVI, was not associated with stream nutrient concentrations for any of the 7 nutrient parameters measured. Our result contrasts with past studies, which demonstrated significant relationships between stream nutrient concentrations and MODIS or Advanced Very High Resolution Radar (AVHRR) derived NDVI measures (Chu et al., 2013; Griffith et al., 2002; Singh et al., 2013). Singh et al. (2013) characterized seasonal variation of vegetation in spring, summer and fall using 42 variables derived from five MODIS products and found that 70-86% of the annual variation in NO_3^-+NO_2^- concentrations was explained by 16 variables describing vegetation, whereas 29-59% of the variation in dissolved phosphorus (DP) concentrations was explained by 12 significant variables. Likewise, using one off water quality samples to examine the interrelationship between 290 individual stream nutrient concentrations collected during the late spring and summer and multiple NDVI and vegetation phenological metrics Griffith et al. (2002) found that nitrate concentrations were significantly associated with mean NDVI for watersheds in the western corn belt ecoregion during late April and early June and that TP concentrations were significantly related with mean NDVI in the Sand Hills ecoregion during late April and mid-June. In comparison, our study paired water quality samples with mean NDVI for the catchment however, no significant relationships were identified that could be used to link the seasonal trends in water quality to vegetation conditions described by NDVI. Our results were potentially influenced by the dry climate conditions of our sample season which would influence role of vegetation in limiting the transport of nutrients and sediment to the stream. Further explanation for our lack of significant results associations may be related to the minimal variability in mean catchment NDVI observed among our catchments. Singh et al. (2013) suggested that homogeneity of land use and land cover among site catchments may be a potential limiting factor of the use of NDVI for classification of seasonal variation in water chemistry. As our region was predominantly composed of row crop agriculture (>60%) and the spatial resolution of the MODIS data was fairly coarse (250m), we potentially were unable to capture finer scale conditions that may have influenced nutrient attenuation by vegetation on the landscape. Taken at face value, however, our results suggest that stream nutrient concentrations are not influenced by temporal variation in vegetation condition when quantified solely by NDVI. Further studies, emphasizing the use of multiple metrics of vegetation in assessing the relationship between stream nutrients variability and catchment scale vegetation condition are needed though to confirm our conclusions.

Linear regression models identified STP's as the dominant land use factor accounting for the observed variability in stream nutrient concentrations of nitrogen and phosphorus forms for our study streams. Specifically, the population served per km^2 by a sewage treatment plant alone accounted for 25% of TN variation and 37% of TP variation for our 29 sample streams. Findings from our derived TN and TP models are in contrast to several previous studies whose results suggest stream concentrations of TN and TP are most strongly related to the amount of agricultural land cover in the catchment (Allen, 2004; Carpenter et al., 1997; Chambers et al., 2008b; Copper et al., 1993; Jones et al., 2001; Withers et al., 2008). In a region similar to our study, Chambers et al. (2008) identified that TN and TP concentrations in 177 streams of SWO were associated with the percent of cropland in the catchment, and identified a rapid increase in TN and TP concentrations with increases in the % cropland above 82%. Results from Chambers et al. (2002) are consistent with findings by Omernik (1976) and Hill et al. (2010) who also observed associations between stream concentrations of TN and TP with increasing agricultural activity in the drainage basin. These studies have frequently linked the association between agricultural land cover and stream nutrients to enriched runoff resulting from the application of fertilizer and manure (Billy et al., 2013; Withers et al., 2003). The key difference between the above mentioned studies and ours is that these studies have focused on nonpoint sources of land use and their study regions captured larger gradients of land use. Further explanation for the difference between our findings and these other studies is that our study occurred during a dry year and experienced low precipitation and low stream flow conditions. Under low rainfall conditions stream flow decreases and there is a decrease in overland flow and runoff that potentially limits the transport of nutrients from agriculture sources to the river system (Carpenter et al., 1998; Klose et al., 2012; Paul & Meyer, 2001; Withers et al., 2003; Yuan et al., 2013). During these low flow conditions the influence of point sources becomes also important as effluent comprises a greater proportion of stream flow and is consequently diluted less than in years with greater flow (Dubrovsky et al., 2010; Johnson et al., 1997; Neal et al., 2010; Withers et al., 2002). For example, Neal et al. (2010) found that under low flow conditions STP effluent discharge was the key source of dissolved phosphorus but under high flow conditions runoff resulted in an increase of stream particulate phosphorus concentrations from nonpoint sources. Similarly, stream SRP and TP concentrations have been traced to STP's where TP loadings in sewage effluent were similar to riverine TP loads under low and intermediate flow conditions in tributaries of the Cuyahoga River in Ohio (Yuan et al., 2013). Given that the population served per km^2 by an STP, rather than agriculture, is identified as the driver of stream TN and TP concentrations, we suggest that landscape drivers of stream nutrient concentrations were limited by the lack of rainfall during our sample season. Furthermore, results from our study suggest that point sources, such as waste water treatment facilities, play a key role in increasing regional stream nutrient concentrations under low flow conditions when stream flow may dominated by wastewater effluent.

Similar to the TN and TP models, the population served per km^2 was significantly associated with stream TKN and SRP concentrations. However, we also found the percent of agriculture in a 30m stream buffer area along the reach 600 m upstream from the sample site was important. Our results suggest that agricultural intensity varies spatially among our study streams, and for the agriculture land use descriptor variables we only observed substantial variability (CV=0.83) within the 30m riparian buffer 600m upstream from the sample site. Proximal agricultural lands and associated activities can contribute disproportionate amounts of both nitrogen and phosphorus (Dodds & Oakes, 2008; Fleming et al., 2002; Kleinman et al., 2002; Paul & Meyer, 2001; Smith et al., 1999); for example nutrients can enter streams directly during fertilizer application of proximal lands or by direct access of livestock grazing in the stream corridor (Baker et al., 1985; Withers et al., 2003; Withers et al., 2009). Fertilizer and manure application that coincides with rainfall events are known to result in an even greater increase of stream SRP and TKN concentrations (Hunsaker et al., 1995; Withers et al., 2003; Yuan et al., 2013). In streams with riparian zones that are dominated by agricultural practices these nutrients can potentially be transported to the stream through runoff, erosion and sub surface flow due to the proximity of the source to the stream (Dodds & Oakes, 2008; Fleming et al., 2002; Kleinman et al., 2002; Paul & Meyer, 2001; Smith et al., 1999). Conversely, by adopting management practices that establish riparian buffer zones near the stream, the direct impacts from agriculture and livestock density can be mitigated (Paul & Meyer, 2001; Tuppad et al., 2010; Sliva & Williams, 2001; Wang et al., 2002). The observed relationship suggests the spatial location of agricultural management practices influences nutrient loss resulting in the addition of SRP and TKN to nearby stream and thus supports calls by previous studies that riparian areas should be targets for reestablishment of natural vegetation cover.

Our results also found that stream SRP and TKN concentrations were linked to point sources, in particular, the population served per km^2 by an STP. These results are similar to results reported by Jarvie et al. (2006) who linked variability of stream SRP concentrations to STP effluent using a boron tracer, and also found that the concentration of SRP is greatest under low flow conditions. Concentrations of SRP and TKN can further be linked to the level of waste water treatment (primary, secondary, tertiary or lagoon) and the frequency of discharge events from lagoon systems (Chambers et al., 2008a; Fleming & Ford. 2002; House & Denison, 1997; Withers et al., 2009). The removal of nutrients from waste water varies between treatment levels with phosphorus removal below 50% for primary, secondary and lagoon systems; however, tertiary treatment can remove upwards of 90% of phosphorus (Freedman, 1995; Wang et al., 2002). In our study, we did not differentiate between levels of treatment for STP's between our sites. However, varying levels of treatment likely influenced the quality and quantity of effluent discharged into our study streams and thus the strength of association we identified between stream nutrients and the population served per km^2 by an STP (Chambers et al., 2008a; Freedman, 1995; Fleming et al., 2002). We can speculate that the strength of our models may be improved with the addition of finer scale STP descriptors that capture the variability of STP effluent quality and quantity giving us a more thorough understanding of the effects of waste water on water quality in southwestern Ontario (Fleming et al., 2002). Further study directed towards examining the effects of STP treatment level on receiving waters is required to understand the variability of stream nutrients in anthropogenically altered systems.

Similar to the above mentioned nutrients, the population served per km^2 by a STP was linked to the stream concentration of NH_3. However, the percent of agriculture in the catchment was negatively associated with stream NH_3. Our results are consistent with previous studies that have found a positive association between STP wastewater and elevated NH_3 concentrations (Miles et al., 2003; Sanchez-Perez et al., 2009; Wang et al., 2013). In an ecological risk assessment conducted by Cotman et al. (2001) elevated stream concentrations of NH_3 were found in receiving waters downstream from municipal STP's resulting in potentially toxic conditions for invertebrates and fish (Constable et al., 2003; Cotman et al., 2001). Findings from our study suggest that STP effluent is a main driver of stream NH_3 concentrations where a complex relationship between temperature, dissolved oxygen and pH affects its toxicity.

Past studies have also found NH_{4-} to be negatively correlated with the percent of agriculture in the catchment during spring, summer and fall seasons (Sliva et al., 2001; Zhang et al., 2008). In these seasons, drier conditions lead to lower water tables enhancing in soil nitrification rates leading to rapid conversion of NH_3 to NO_3^-+NO_2^- following application of fertilizers to agricultural lands (Dubrovsky et al., 2010; McMahon et al., 2008). Under these conditions there is also an increased opportunity for NH_3 to be volatilized into the atmosphere or assimilated by vegetation on the landscape thereby reducing transport to streams (Johnson et al., 2005; Vitousik et al., 1997). This hypothesis is supported by Vadas and Powell (2013) who identified NH_3 concentrations to be linked to manure application immediately prior to high storm events where an increased severity of storms contributed to the greatest increases in NH_4^- loss due to runoff and erosion for up to two weeks after the application of manure on agricultural lands. As the sampling frequency of our study did not target events, but rather captured the ambient conditions in our streams under a dry year, it is unlikely that we collected samples representative of runoff events. Sampling to incorporate more temporal variability in stream NH_3 concentrations in future studies could thus improve our model strength by demonstrating the relationship between stream NH_3 concentrations and the timing of fertilizer application with rainfall events.

Nitrate-nitrite was the only nutrient parameter not associated with the presence of STP's in the catchment, but instead was significantly related to the percent of agriculture and urbanization in the catchment. Agriculture and to a lesser extent urban are known to be sources of nitrate due to the application of fertilizers to promote crop growth (Dubrovsky et al., 2010). In Southwestern Ontario, estimated nitrogen losses from agriculture are between 10-20 kg of N/ha and the region is classified as being at high or very high risk of nitrogen contamination by the Indicator of the Risk of Water Contamination by Nitrogen (IROWC-N) based on agricultural land management practices (Lefebvre et al., 2005). Heavy fertilization of industrial crops (corn, potatoes, wheat) or urban green spaces (private lawns, golf courses) may result in excess fertilizer retained in soils in the form of nitrate (Dubrovsky et al., 2010). Nitrate is highly soluble becoming mobilized by rainfall and leaching into ground water where it accumulates and remains relatively stable in shallow aquifers (Burow et al., 2010; CCME, 2012; Dubrovsky et al., 2010). Studies in our region have shown that nitrate concentrations in groundwater are elevated and associated with heavy fertilization and agricultural activity in the area (Haslauer et al., 2004). Groundwater flow to streams may thus act as an important source of nitrate, contributing to a long term legacy effect of agricultural practices (Dubrovsky et al., 2010). The dry conditions of our study year may have resulted in nitrate rich groundwater supplies acting as the main source of stream base flow, contributing to the differences between our TN and NO_3^-+NO_2^- models.

5.1 Model Performance

Evaluation of model performance indicated that the assessed models successfully predicted stream nitrogen concentrations but not phosphorus. Model strength did not appear to influence model performance as SRP and TP models exhibited R^2 values greater or similar to R^2 values for TN and NO_3^-+NO_2^- models. The differences in predictive performance of our models may be attributable to interactions between inter-annual differences in precipitation and land management practices (e.g., crop rotation, tillage, livestock density, manure storage, fertilizer application) not captured in our models having greater influence on stream phosphorous than nitrogen concentrations (Banner et al., 2009; Buck et al., 2004; Einheuser et al., 2013; Niraula et al., 2013).

Inter and intra-annual variability in rainfall is known to control the transport of nutrients from landscape sources to streams, by increasing sub-surface flow, erosion and runoff. Heathwaite et al. (2000) described how phosphorus loss is more limited by transport factors such as runoff and sub-surface flow compared to nitrogen loss through leaching of water soluble nitrate. Baker et al. (1985) also found that the practice of row cropping increased the potential for erosion and surface runoff, processes which are associated with sediment bound phosphorus and linked to increases stream phosphorus concentrations. Similarly, precipitation influences the quality and volume of sewage effluent discharged into receiving streams. Among our streams the population served per km^2 by an STP had the greatest variability among our descriptor variables. However, the 21 streams in this study that received sewage effluent varied substantially in terms of the level of treatment, including sewage lagoons, as well as primary, secondary and tertiary treatment. Effluent treatment level has been shown to be strongly associated with nutrient removal (Freedman 1995). For example, primary treatment facilities remove between 5% and 15% of phosphorus whereas removal in tertiary treatment systems facilities is upwards of 90% (Freedman, 1995). Likewise, the efficiency of treatment lagoons depends on biological productivity of these systems and is strongly influenced by climate factors (Chambers et al., 2008a). Hickey et al. (1989) found high levels of ammonia, inorganic nitrogen and reactive phosphorus varied between summer and winter grouped samples at individual lagoons but also found substantial variation of nutrient concentrations among individual lagoon systems and suggested that climate variables (precipitation, sunlight, wind, etc.) affect biological processes and microbial activity that influences effluent quality. Heavy rainfall events may substantially increase the volume of waste water in lagoons, overwhelming their capacity, resulting in the reduction of treatment efficiency and the discharge of partially treated waste water during high flows. Lagoon facilities typically discharge during the spring or late fall when stream flows are higher, to aid in the dilution of nutrients from the waste water (Neal et al., 2010; Sanchez-Perez et al., 2009; Yuan et al., 2013); however, under low volume conditions or in dry year, lagoons may not release effluent during a season resulting in great inter-annual variation of discharge from point sources. Unlike lagoon systems, mechanical facilities continually discharge throughout the year with varying quality and volumes of waste water. Examination of annual wastewater reports from facilities that discharge in our study streams found that the effluent nutrient concentrations and volumes vary between years for all facilities in our study region. Similar to lagoon systems, intense precipitation events can result in overflow and bypass during the pre-treatment stage of mechanical facilities and may release untreated sewer water into receiving streams. Intermittent bypass events discharge untreated effluent that may increase stream nutrient concentrations in receiving water dependent on the flow conditions of the stream (Chambers, et al., 2008b; Cooke et al., 2009). The described intra- and inter-annual variations in land management practices and STP effluent discharge and the inherent interaction of rainfall may have influenced our models ability to capture nutrient variability. Further studies are required at to establish if model performance could be improved by incorporating the effects of land management practices and STP effluent volume and quality on the temporal variability of stream nitrogen and phosphorus concentrations.

Results of the model performance evaluation suggest that despite modest R^2-values our N models were able to predict average TN and NO_3^-+NO_2^- concentrations about 80% of the time. This finding suggests that our models could be used to predict regional effects of current land use and future land use change on stream nitrogen concentrations. However, it must be noted that our results showed that the nitrogen models were best able to predict nitrogen concentrations around the mean of the data used to derive the models (5 mg/L) and consistently predicted concentrations at evaluation sites where TN concentrations ranged from 3 mg/L to 7 mg/L. The further an evaluation concentration was outside of this range the less likely it was for the model to successfully predict the expected TN concentration. This pattern in model performance suggests that the model may only be robust within approximately one standard deviation (± 2.4 mg\L) of the mean of the data used to derive the model. Results from the NSE index further suggest that our model lacked robustness much beyond the mean as the resultant scores (NSE= -0.25) suggested that the observed mean was as good or better a predictor of nitrogen concentrations than our models. Indeed, examination of our individual site O:E scores showed that sites 30-Nanticoke Creek and 33-Upper Thames River were not successfully predicted under any of the five model evaluation scenarios. Average nitrogen concentrations at Nanticoke creek were consistently outside of the lower bound of our model training data (TN = <1.8 mg/L , NO_3^-+NO_2^- =<1.48 mg/L). In contrast, concentrations at the 33-Upper North Thames River exhibited the highest concentrations among all evaluation streams and were consistently outside than the upper bound of our model training data (TN = >8.72mg/L, NO_3^-+NO_2^- = >9.5mg/L). Further examination of evaluation site performance revealed that site 30-Nanticoke Creek and site 33-Upper Thames River also lay in the outer range of the land use gradients. 30-Nanticoke Creek was at the lower range of land use gradients with 2% urban and 72% agriculture; whereas the 33-Upper Thames River demonstrated land use at the upper bound of the range of the land use gradients with 2% urban and 92% agriculture. Furthermore, visual inspection of 30-Nanticoke Creek revealed differences in surface geology compared to other streams studied that may have influenced geochemical processes in the stream (Freedman, 1995). Similarly, our site on the 33-Upper Thames River was less than 200 m downstream from the outflow point of the Mitchell waste water lagoon where effluent is likely to be highly concentrated. These 2 sites appear to be unique and may not be totally representative of the more extreme conditions leading to the poor predictive performance by our models. Further studies are needed that capture a longer gradient of nitrogen concentrations to confirm the utility of our nitrogen models as a predictive tool.

6 Management application and implications

Findings from our study indicate that rivers in southwestern Ontario are experiencing degradation in water quality associated with intensifying land use. Our findings clearly identify a high rate of exceedances in stream nutrient concentrations of the provincial and national water quality objectives/guidelines for the protection of aquatic species life. For example, high (>0.03mg/l) concentrations of phosphorus are associated with the eutrophication of water bodies that can impact drinking water quality, recreational access, aquatic habitat, and ultimately lead to fish kills due to deoxygenated zones. Although ammonia is naturally occurring in aquatic environments, it can be toxic for fish and other organisms if concentrations are >0.1mg/l. Whereas nitrate concentrations in our streams studied fell within the targeted objectives for all samples with the exception of late spring (June 3, 2012), NH_3 and TP were found on average to exceed CEQG and provincial objectives in >5 of the 10 samples collected at each site during our May through November sample season. Most worrisome are one off measures of NH_3 and TP concentrations during summer samples that were >600x the national objective for NH_3 and were >100x the provincial objective for TP. The concentrations of nitrogen and phosphorus measured in our streams indicated that nutrient concentrations are a potential risk factor for water quality and the health of aquatic ecosystems (Appendix E). Our findings demonstrate the need to address the number of exceedances above PWQO and CEQG through long and short term management strategies of water quality in southwestern Ontario streams.

Our project identified key drivers of stream nutrient concentrations with the goal of providing empirically derived data to act as a foundation for science-based management of water quality in SWO. The population served per km^2 by STP's and percent agriculture in the catchment were associated with nitrogen and phosphorus concentrations in our streams. Specifically, we found that of the 29 streams studied those receiving effluent from STP's were most often exceeded water quality objectives throughout our sampling season indicating a need for future monitoring of nutrient parameters downstream from STPs. We identified 5 sites in particular that consistently

(>90% of samples) exceeded PWQO for NH_3 and TP; 2-Avon River below the Stratford WWTP, 13-Canagagigue creek (Elmira WWTP), 51-Catfish Creek (Alymer lagoon); 40-South Thames River (Woodstock WWTP and Tavistock lagoon); and 23-Kettle Creek (Belmont lagoon). Many of the other streams sampled that had a high rate of exceedances (>70% of samples) also contained STP in their catchment suggesting that current treatment infrastructure is not meeting water quality objectives. Based on these findings it is likely that many of the current treatment systems require monitoring of water quality in receiving waters upstream and downstream of the facility to identify the potential influence of discharged effluent on water quality. Our study also identified that improving water quality also requires changes in the management of agricultural and urban lands. Specifically it is likely that further implementation of Best Management Practice's (BMPs) are needed to mitigate nutrient loss from high intensity agriculture lands. Past studies have found that BMPs can significantly improve water quality and limit the transport of nutrient rich soil and water from the landscape to the stream (Johnson et al., 1997; Omernik et al., 1981; Tuppad et al., 2010; Wang et al., 2002). Riparian buffer zones have long been considered instrumental in attenuating nutrients on the landscape and minimizing erosion and runoff, thus limiting the transport of nutrients to the stream (Basnyat et al., 2000; Dodds et al., 2008; Iniguez-Armijos et al., 2014; Richards et al., 1996; Sliva et al., 2001). Based on our findings there is a need for improved land management practices in order to protect and enhance water quality in southwestern Ontario streams.

The findings from our study demonstrate the utility of land use as a predictive tool for stream nutrient concentrations. In particular, our nitrogen models quantified sources from land use to stream nitrogen concentrations in catchments located in southwestern Ontario draining into the Great Lakes Basin. Our models provide opportunities for planners and managers to better understand the impacts of land use and development on water quality in southwestern Ontario. Our nitrogen models could potentially be used by planners as predictive tools to improve their understanding of the effects that changes in land use have on water quality. Evaluation of model performance however, suggests that to be used as a predictive tool, our models require the inclusion of a larger gradient of variables to improve the predictive performance for streams with nutrient concentrations greater than one standard deviation from the mean of the training data. Improving the predictive performance of our models would allow planners the opportunity to assess the potential impact of land use development strategies on water quality. Furthermore, through the prediction of stream nitrogen managers are able to identify potential source areas and thus enable the targeting of management efforts towards the most important source areas allowing more cost-efficient and effective mitigation of the effects of current land use practices. Managers are then able to project potential outcomes based on mitigation actions and use these projections as performance measures. Overall, our nitrogen models are a cost saving mechanism for planners and managers to use that enables them to make informed decisions based on model projections enabling effective management of regional water quality.

7 Future research

Findings from my research show that STP and land use in the catchment as well as proximal to the stream can be used with some success to predict stream nitrogen concentrations. However, the performance of models derived using simple land use metrics may be limited due to the temporal and spatial variability of nutrient concentrations in the streams studied. Among our streams we measured high seasonal variability in stream nitrogen and phosphorus concentrations between the 10 samples collected during the May through November sampling period, however our findings showed no association between NDVI and stream nutrient concentrations. The homogeneity of the landscape, as measured by the NDVI, likely did not capture variability in land cover that could explain seasonal variation in stream nutrient concentrations. Therefore, the use of multiple metrics of vegetation condition including measures of greenness, soil reflectivity, soil moisture, etc should be explored to better capture the seasonal variation of land cover that has been shown to influence the mobilization and assimilation of nutrients on the landscape (Basnyat et al., 2000; Griffith et al., 2002). Although NDVI measures vegetation condition, it is the interaction between multiple dynamic processes (climate, rainfall, soil type, soil moisture, photosynthetic activity, etc.) that drives nutrient cycling on the landscape and enables the mobilization of nutrients for transport to the stream. By incorporating multiple measures of land cover we can begin to understand the relationship between the dynamic processes described through land cover metrics and the temporal variation of stream nutrients. This relationship is important for assessing seasonal variation of stream nutrients and developing models that reflect these seasonal changes. Therefore, future modeling of stream nutrient concentrations needs to account for the temporal variability of nitrogen and phosphorus to determine if the model performance could be improved through seasonally based prediction.

The second consideration for future research that needs to be addressed is the effects of finer scale management practices on stream phosphorus concentrations. Our study produced phosphorus models that were of similar strength to the nitrogen models yet were unable to predict May through November average phosphorus concentrations in evaluation streams under any of the evaluation scenarios. It may be that finer scale management practices are driving the variability associated with phosphorus concentrations but are poorly captured by coarse descriptions of land use. This hypothesis is supported by studies of small agricultural streams in southern Ontario that have recently found that among stream variability in stream phosphorus concentrations is linked to the use of farm scale management practices (Barton et al., 1997; Yates et al., 2006a; Yates et al., 2007). However, there is a lack of studies on the larger streams and small rivers of the size used in our study. As such further research studies need to assess the relative importance of fine scale management practices (tillage, row cropping, fertilizer application, etc.) in both urban and agricultural lands at larger spatial scales. Results of these studies would assist in determining if the inclusion of fine scale management practices would improve the predictive performance of phosphorus models in multiple evaluation scenarios in southern Ontario streams.

Findings from our study identified that future research needs to be directed towards quantifying the volume and the quality of effluent discharged from STP to better understand the potential effects of the level of treatment on stream nutrient concentrations. Our study described waste water point sources using a distance measure as well as the populations served by a STP per km^2. However, neither metric describes the variability in effluent quality associated with the level of treatment nor the quantity of effluent discharged into receiving waters by STP's. Although the population served by a STP was found to be significantly related to our stream nitrogen and phosphorus concentrations, we were unable to determine what it is about the STP that needs to be addressed to improve water quality in receiving streams. Qualitatively the effects of STP do not appear to be associated with treatment level. For example, severely impaired water quality was observed in Kettle Creek which was exposed to a lagoon system but also the Avon and Thames Rivers which have tertiary level treatment. As such we are unable to identify if wastewater is being discharged pre-emptively or if increasing demands on infrastructure due to population growth require the STP to be upgraded to improve effluent quality. Effluent data can be obtained (albeit with some difficultly) from all regional STPs as Provincial regulations require that facilities test effluent water quality prior to discharge and to monitor facility's compliance. Future work should integrate the available effluent quality and quantity data into models to determine if a better understanding of the effects of waste water on the temporal variability of stream nutrients can be achieved.

Finally, future research needs to determine if a longer gradient of stream nitrogen concentrations would improve model performance under multiple scenarios. Our study developed nutrient models using coarse scale land use descriptors to predict stream nutrient concentrations and identified that model performance is limited when observed nitrogen concentrations of evaluation streams are >1 standard deviation from the mean. Therefore, our nitrogen model performances may be improved by incorporating a larger number of streams that encompasses a longer gradient of nitrogen concentrations in the model training data. In addition, the newly derived models would need to undergo an evaluation of model performance to determine the utility of the model as a predictive tool. Incorporation of data provided by the PWQMN for the development of these models may alleviate pressures due to economic and time constraints and also allow for the models to be evaluated over a greater variety of streams.

8 Conclusions

Stream nutrient concentrations in southwestern Ontario are highly variable, yet are comparable to concentrations found in streams with similar regional characteristics. Agriculture and municipal waste water were found to be important drivers of stream nutrients concentrations in streams located in southwestern Ontario. Results from this study indicate that the variability of stream nutrient concentrations may be attributed to differences in land use among catchments. Among our models the population served per km2 by a STP's was identified as the most predictive source of stream nutrients. Although model strength was similar between nitrogen and phosphorus models, evaluation of model performance found that the nitrogen models outperformed phosphorus models under all scenarios. Nitrogen models were able to successfully predict on average 70% of evaluation sites, in contrast, phosphorus model performance was poor, suggesting that the phosphorus exhibits greater variability related to land use. Additional efforts may be needed to identify drivers of the temporal variation of phosphorus using finer scale management practices. Future research examining the relationships between land use and stream nutrient concentrations needs to develop a better understanding the temporal variability of nutrients and assess model performance to determine how and if the derived models can be applied for land and water quality management.

9 References

Agriculture and Agri-food Canada (2012). Crop Inventory Map (*UTM17N*). Retrieved from ftp://ftp.agr.gc.ca/pub/outgoing/aesb-eos-gg/Crop_Type_Mapping/2012/

Agriculture and Agri-food Canada (2011). Crop Inventory Map (*UTM17N*). Retrieved from ftp://ftp.agr.gc.ca/pub/outgoing/aesb-eos-gg/Crop_Type_Mapping/2011/

Alexander, R. B., Smith, R. A., Schwarz, G. E., Boyer, E. W., Nolan, J. V., & Brakebill, J. W. (2008). Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi river basin. *Environmental Science & Technology, 42*(3), 822-830. doi: 10.1021/es0716103

Allan, J. (2004). Landscapes and riverscapes: The influence of land use on stream ecosystems. *Annual Review of Ecology Evolution and Systematics, 35*, 257-284. doi: 10.1146/annurev.ecolsys.35.120202.110122

Arhonditsis, G.B., & Brett, M.T. (2004). Evaluation of the current state of mechanistic aquatic biogeochemical modeling, *Marine Ecology Progress Series*, 271, 13-26

Baker, A. (2003). Land Use and Water Quality. *Hydrological Processes*, 17, 2499-2501. DOI: 10:1002/hyp.5140

Baker, D. (1985). Regional water-quality impacts of intensive row-crop agriculture - A Lake Erie basin case-study. *Journal of Soil and Water Conservation, 40*(1), 125-132.

Banner, E., Stahl, A.J., Dodds, W.K. (2009). Stream discharge and riparian land use influence in-stream concentrations and loads of phosphorus from central plains watersheds, *Environmental Management, 44*:552-565

Barton, D.R. (1996). The use of Percent Model Affinity to assess the effects of agriculture on benthic invertebrate communities in headwater streams of southern Ontario, Canada. *Freshwater Biology, 36*:397–410

Barton, D. R. & Farmer (1997). The effects of conservation tillage practices on benthic invertebrate communities in headwater streams in southwestern Ontario, Canada. *Environmental Pollution, 96*: *2*, 207–215

Basnyat, P., Teeter, L., Lockaby, B., & Flynn, K. (2000). The use of remote sensing and GIS in watershed level analyses of non-point source pollution problems. *Forest Ecology and Management, 128*(1-2), 65-73. doi: 10.1016/S0378-1127(99)00273-X

Billy, C., Birgand, F., Ansart, P., Peschard, J., Sebilo, M., & Tournebize, B. (2013). Factors controlling nitrate concentrations in surface waters of an artificially drained agricultural watershed, *Landscape Ecology*, 28:665-684, DOI 10.1007/s10980-013-9872-2

Buck, O., Niyogi, D.K & Townsend, C.R (2004). Scale-dependence of land use effects on water quality of streams in agricultural catchments, *Environmental Pollution*, Volume 130, Issue 2, July 2004, Pages 287–299

Burow, KR., Bernard T. Nolan, Michael G. Rupert, and Neil M. Dubrovsky (2010). Nitrate in Groundwater of the United States, 1991−2003, *Environmental Science & Technology*, 44 (13), 4988-4997

Carpenter, S., Caraco, N., Correll, D., Howarth, R., Sharpley, A., & Smith, V. (1998). Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications, 8*(3), 559-568. doi: 10.2307/2641247

Canadian Council of Ministers of the Environment (CCME)(2012). Canadian water quality guidelines for the protection of aquatic life: Nitrate. In: Canadian environmental quality guidelines, Canadian Council of Ministers of the Environment, Winnipeg, MB, Canada.

Canadian Council of Ministers of the Environment (CCME)(2010). Canadian water quality guidelines for the protection of aquatic life: Ammonia, Canadian guidance framework for the management of freshwater systems. In Canadian Council of Ministers of the Environment (ed.) Canadian environmental quality guidelines, 2009. Canadian Council of Ministers of the Environment, Winnipeg, MB, Canada.

Canadian Council of Ministries for the Environment (CCME), April 2009 (Revised 2012) Protocols Manual for Water Quality Sampling in Canada, PN 1461. Retrieved from: http://www.ccme.ca/assets/pdf/protocols_document_e_final_101.pdf

Canadian Council of Ministers of the Environment (CCME)(2004). Canadian water quality guidelines for the protection of aquatic life: Nitrogen, Canadian guidance framework for the management of freshwater systems. In Canadian Council of Ministers of the Environment (ed.) Canadian environmental quality guidelines, 2004. Canadian Council of Ministers of the Environment, Winnipeg, MB, Canada.

Canadian Council of Ministers of the Environment (CCME)(2004). Canadian water quality guidelines for the protection of aquatic life: Phosphorus, Canadian guidance framework for the management of freshwater systems. In Canadian Council of Ministers of the Environment (ed.) Canadian environmental quality guidelines, 2004. Canadian Council of Ministers of the Environment, Winnipeg, MB, Canada.

Chambers P.A., Allard, M., Walker, S.L., Marsalek, J., Lawrence, J., Servos, M., Busnarda, J., Munger, K.S., Adare, K., Jefferson, C., Kent, R.A., & Wong, M.P..

(1997). The impacts of municipal wastewater effluents on Canadian waters: a review. *Water Quality Research.Journal, Canada*, 32: 659-713.

Chambers, P.A., Mark Servos, M., Macdonald, R., Van Der Kraak, G. (2008a). Threats to Sources of Drinking Water and Aquatic Ecosystem Health in Canada, Environment Canada, Municipal Wastewater Effluents, Retrieved from https://www.ec.gc.ca/inre-nwri/default.asp?lang=En&n=235D11EB-1&offset=10&toc=show

Chambers, P.A., Vis, C.C., Brua, R.B., Guy, M.M., Culp, J.M., & Benoy, G.A. (2008b). Eutrophication of agricultural streams: defining nutrient concentrations to protect ecological condition. *Water Science & Technology, 58*(11), 2203-2210. doi:10.2166/wst.2008.815

Chambers, P. A., McGoldrick, D. J., Brua, R. B., Vis, C., Culp, J. M., & Benoy, G. A. (2012). Development of environmental thresholds for nitrogen and phosphorus in streams. *Journal of Environmental Quality, 41*(1), 7-20. doi: 10.2134/jeq2010.0273

Chu, Hone-Jay, Liu Chun-Yu & Chi-Kuei Wang (2013). Identifying the Relationships between Water Quality and Land Cover Changes in the Tseng-Wen Reservoir Watershed of Taiwan, *International Journal of Environ. Research and Public Health, 10, 478-489, doi:10.3390/ijerph10020478*

Constable, M., Charlton, M., Jensen, F., McDonald, K., Craig, G., &.Taylor,, K.W. (2003). An ecological risk assessment of ammonia in the aquatic environment. *Human and Ecological Risk Assessment*, 9(2), 527-548. Retrieved from http://search.proquest.com/docview/200048681?accountid=15115

Cooke, S., Wilson, J.**,** Dubrick, B., Ellis,J., Elder, K. Kerr, J., Murray, D., Laird, J., Walsh, C., Wheeler, G, Davidson, A., Sharp, E., Mungar, P., Spiers, T., Kongara, S., Williamson, G., Garibaldi, B., Slater,C., Davis, K. Guelph; Kodousek, N., Mehmood, K. Region of Waterloo; District Office, Ministry of the Environment, Ethier, M. Ontario Clean Water Agency, Austin, J. City of Cambridge (2009). *Best Practices: Municipal Wastewater Treatment Plant Bypass and Spill Prevention & Reporting in the Grand River Watershed*, Retrieved from: Grand River Municipal Water Managers Working Group, http://www.grandriver.ca/governance/spillreport2009.pdf

Cotman, M., Zagorc-Koncan, J.. & Droic, A. (2001). Study of impacts of treated wastewater to the Krka river, Slovenia, *Water Science & Technology, 44*:6, 47–54

Crins, W.J., Gray, P.A., Uhlig, P., & Wester, M.C. (2009). The Ecosystems of Ontario, Part 1: Ecozones and Ecoregions, Science and Information Branch, Inventory, Monitoring and Assessment Section, The Ontario Ministry of Natural Resources, Retrieved from:

http://www.mnr.gov.on.ca/en/Business/ClimateChange/Publication/STDPROD_101589.htm

Cunha, D.F., Dodds, W. K., & Calijuri, M. (2011). Defining nutrient and biochemical oxygen demand baselines for tropical rivers and streams in Sao Paulo state (Brazil): A comparison between reference and impacted sites. *Environmental Management*, *48*(5), 945-956. doi: 10.1007/s00267-011-9739-8

Davies-Colley, R., Hickey, C., & Quinn, J. (1995). Organic-matter, nutrients, and optical characteristics of sewage lagoon effluents. *New Zealand Journal of Marine and Freshwater Research*, *29*(2), 235-250.

Dodds, W. K., & Oakes, R. M. (2008). Headwater influences on downstream water quality. *Environmental Management*, *41*(3), 367-377. doi: 10.1007/s00267-007-9033-y

Dodds, W. K., Robinson, C. T., Gaiser, E. E., Hansen, G. J. A., Powell, H., Smith, J. M., Morse, N.B., Johnson, S.L., Gregory, S.V., Bell, T., Kratz, T.K., & McDowell, W. H. (2012). Surprises and insights from long-term aquatic data sets and experiments. *Bioscience*, *62*(8), 709-721. doi: 10.1525/bio.2012.62.8.4

Dolan, D.M., & Chapra, S.C. (2012). Great Lakes Total Phosphorus revisited: Loading analysis and update (1994–2008), *Journal of Great Lakes Research, 38,* 730–740

Dubrovsky, N.M., Burow, K.R., Clark, G.M., Gronberg, J.M., Hamilton P.A., Hitt, K.J., Mueller, D.K., Munn, M.D., Nolan, B.T., Puckett, L.J., Rupert, M.G., Short, T.M., Spahr, N.E., Sprague, L.A., & Wilber, W.G., (2010). The quality of our Nation's waters—Nutrients in the Nation's streams and groundwater, 1992–2004: *U.S. Geological Survey Circular*, 1350, 174 p. Additional information about this study is available at http://water.usgs.gov/nawqa/nutrients/pubs/circ1350

Einheuser, M. D., Nejadhashemi, A. P., & Woznicki, S. A. (2013). Simulating stream health sensitivity to landscape changes due to bioenergy crops expansion. *Biomass and Bioenergy*, 58(0), 198-209. doi:http://dx.doi.org/10.1016/j.biombioe.2013.08.025

Environmental Protection Agency (EPA). Washington, DC (2004). Primer for Municipal Waste water treatment Systems. Document no. EPA 832-R-04-001.

ESRI (Environmental Systems Resource Institute). (2010a). ArcMap 10.0. ESRI, Redlands, California.

ESRI (Environmental Systems Resource Institute). (2010b). ArcHydro 2.0. ESRI, Redlands, California.

Fleming, R. % Ford, M. (2002). Comparison of storage, treatment, utilization, and disposal systems for human and livestock wastes, Available online at: http://www.ridgetownc.uoguelph.ca/research/documents/fleming_wastes.PDF. Date accessed: October1, 2014.

Freedman, Bill (1995). Environmental Ecology, Second Edition: The Ecological Effects of Pollution, Disturbance, and Other Stresses, Academic Press Inc. San Diego, CA, pg. 195

Government of Canada, Environment Canada (2012). Great Lakes Nutrient Initiative. Retrieved from http://www.ec.gc.ca/grandslacs-greatlakes/default.asp?lang

Great Lakes Water Quality Agreement (1972). Revised Great Lakes Water Quality Agreement of 1978. As amended by protocol November 18th, 1987. International Joint Commission, Windsor, Ontario =En&n=4FF37866-1

Griffith, J., Martinko, E., Whistler, J., & Price, K. (2002). Interrelationships among landscapes, NDVI, and stream water quality in the US central plains. *Ecological Applications, 12*(6), 1702-1718. doi: 10.2307/3099933

Haslauer, C.P., Rudolph, D.L., Thomson, N.R., Walton, R., & Misek-Evans, M. (2005). Impacts of changing agricultural land-use practices on municipal groundwater quality: Woodstock, Ontario, Bringing Groundwater Quality Research to the Watershed Scale, 297, 223-233

Hawthorne, L.B. (2012). Geospatial Modelling Environment, *Spatial Ecology*. Retrieved from: http://www.spatialecology.com/gme/, 2013

Heathwaite, L., Sharpley, A., & Gburek, W. (2000). A conceptual approach for integrating phosphorus and nitrogen management at watershed scales. *Journal of Environmental Quality*, *29*(1), 158. Retrieved from http://search.proquest.com/docview/197396537?accountid=15115

Heathwaite, A.L., & Dils, R. M. (1999). The controversial role of tile drainage in phosphorus export from agricultural land, *Water Science and Technology*, *39*(12) Page p.55To-61

Hickey, C. W., Quinn, J. M., & Davies-Colley, R. J. (1989). Effluent characteristics of domestic sewage lagoons and their potential impacts on rivers. *New Zealand Journal of Marine and Freshwater Research*, *23*: 585-600.

Hill, B.H., Bolgrien, D.W, Herlihy, A.T, Jicha, T.M., & Ted R. Angradi (2011). A synoptic survey of nitrogen and phosphorus in tributary streams and great rivers of the upper Mississippi, Missouri, and Ohio River basins. *Water, Air, & Soil Pollution*. 216.1-4

House, W.A., & Denison F.H. (1997). Nutrient dynamics in a lowland stream impacted by sewage effluent: Great Ouse, England. *Science of the Total Environment*, *205*:25–49.

Houser, J. N. & Richardson, W. B. (2010). Nitrogen and phosphorus in the upper Mississippi river: Transport, processing, and effects on the river ecosystem. *Hydrobiologia, 640*(1), 71-88. doi: 10.1007/s10750-009-0067-4

Hudon, C., & Carignan, R. (2008). Cumulative impacts of hydrology and human activities on water quality in the St. Lawrence river (Lake Saint-Pierre, Quebec, Canada). *Canadian Journal of Fisheries and Aquatic Sciences, 65*(6), 1165-1180. doi: 10.1139/F08-069

Hunsaker, C. T., & Levine, D. A. (1995). Hierarchical approaches to the study of water quality in rivers. *Bioscience*, 45(3, Ecology of Large Rivers), 193-203. Retrieved from http://www.jstor.org/stable/1312558

Hynes, H. B. N. (1975). Edgardo Baldi memorial lecture. The stream and its valley. *Verhandlungen der Internationalen Vereinigung fur theoretische und angewandte Limnologie, 19*, 1-15.

Iniguez–Armijos, C., Leiva, A., Frede H–G, Hampel, H., & Breuer, L. (2014) Deforestation and Benthic Indicators: How Much Vegetation Cover Is Needed to Sustain Healthy Andean Streams? *PLoS ONE*, 9(8): e105869. doi:10.1371/journal.pone.0105869

Jarvie, H., Neal, C., Withers, P.J. (2006). Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? *Science of the Total Environment*, *360*: 246– 253

Johnson, L.B., Richards, C., Host, G. & Arthur, J.W. (1997). Landscape influences on water chemistry in Midwestern stream ecosystems. *Freshwater Biology, 37(1)*, 193-208. doi: 10.1046/j.1365-2427.1997.d01-539

Jones, K.B., Neale, A.C., Nash, M.S., Van Remortel, R.D., Wickham, J.D., Riitters, R.H., & O'Niell, R.V. (2001). Predicting nutrient and sediment loadings to streams from landscape metrics: a multiple watershed study from the United States Mid-Atlantic Region. *Landscape Ecology, 16* : 301–312.

Jong, R.D., Yang, J.Y., Drury, C.F., Huffman, E., Kirkwood, V., & Yang, X.M. (2005). Water Quality-Nitrogen. Pages 124-130 in Lefebvre, A., W. Eilers, et B. Chunn (eds.). 2005. Environmental Sustainability of Canadian Agriculture: Agri-Environmental Indicator Report Series – Report #2. Agriculture and Agri-Food Canada, Ottawa, Ontario.

Kang, S.J., Olmstead, K.,Takacs, K., & Collins, J. (2008). Municipal Nutrient Removal Technologies Reference Document, U.S. Environmental Protection Agency (EPA) Office of Wastewater Management, Municipal Support Division, Municipal Technology Branch, EPA 832-R-08-006

Kanwar, R.S. (2006). The effects of cropping systems on NO_3^- losses to tile drain, *The Journal of the American Water Resources Association*, 42(6), pp.1493-1501, DOI: 10.1111/j.1752-1688.2006.tb06016.x

Kleinman, P.J., Sharpley, A.N., Barton, M.G., & Elwinger, G.F. (2002). Effect of Mineral and Manure phosphorus sources on runoff phosphorus. *Journal of Environmental Quality*, 31:6, 2026

Klose, K., Cooper, S.D., Leydecker, A.D. & Kreitler, J. (2012). Relationships among catchment land use and concentrations of nutrients, algae and dissolved oxygen in a southern Californian River. *Freshwater Science*, 31(3):908–927, DOI: 10.1899/11-155.1

Krause, P., Boyle, D.P. & Base, F. (2005). Comparison of different efficiency criteria for hydrological model assessment. *Advances in Geosciences*, 5, 89-97, SRef-ID: 1680-7359/adgeo/2005-5-89

Lefebvre, A., Eilers, W., & Chunn, B. (eds.) (2005). Environmental Sustainability of Canadian Agriculture: Agri-Environmental Indicator Report Series – Report #2. Agriculture and Agri-Food Canada, Ottawa, Ontario

Levine, D.M., Stephan, D., Krehbiel, T.C., Berenson, M.L., & Bliss, J.G. (2004).Statistics for Managers, Using Microsoft Excel, Canadian Edition, Pearson Education Canada Inc., Toronto, Ontario

Lillisand, T.M., Kiefer, R.W.& Chipman, J.W. (2008). Remote Sensing and image interpretation, 6th ed., Hoboken, NJ: Wiley & Sons.

Lu, F., Ni, H., Liu, F., & Zeng, E. Y. (2009). Occurrence of nutrients in riverine runoff of the Pearl River delta, south China. *Journal of Hydrology, 376*(1-2), 107-115. doi: 10.1016/j.jhydrol.2009.07.018

McMahon, P.B., Böhlke, J.K., Kauffman, L.J., Kipp, K.L., Landon, M.K., Crandall, C.A., Burow, K.R., & Brown, C.J., (2008), Source and transport controls on the movement of nitrate to public supply wells in selected principal aquifers of the United States: Water Resources Research, v. 44, W04401, 17 p., doi: 10.1029/2007WR006252, accessed June 17, 2010, at http://www.agu.org/pubs/crossref/2008/2007WR006252.shtml.

Michalak, A.M., Anderson, E.J., Beletsky, D., Boland, S., Bosch, N.S., Bridgeman, T.B., Chaffin, J.D., Cho, K., Confesor, R., Daloglu, I., DePinto, J.V., Evans, M.A., Fahnenstiel, G.L., He, L., Ho, J.C., Jenkins, L., Johengen, T.H., Kuo, K.C., LaPorte, E., Liu, X., McWilliams, M.R., Moore, M.R.,. Posselt, D.J., Richards, R.P., Scavia, D., Steiner, A.L. Verhamme, E., Wright, D.M., & Zagorski, M.A. (2013). Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. *Proceedings of the National Academy of Science of the United States of America*, *110*(16), 6448-6452. doi: 10.1073/pnas.1216006110

Morse, N.B., & Wollheim, W.M. (2014). Climate variability masks the impacts of land use change on nutrient export in a suburbanizing watershed. *Biogeochemistry*, 121(1), pp 45-59

Nash, J.E. & Sutcliffe, J.V. (1970). River flow forecasting through conceptual models part I – A discussion of principles. *Journal of Hydrology* 10(3): 282–290.

Natural Resources Canada (2014). Educational Resources, Land Cover and Land Use. Retrieved from: http://www.nrcan.gc.ca/earth-sciences/geomatics/satellite-imagery-air-photos/satellite-imagery-products/educational-resources/9373

Neal, C., Jarvie, H.P., Williams, R., Love, A., Neal, M., Wickham, H., Harman ,S. & Armstrong, L. (2010). Declines in phosphorus concentration in the upper River Thames (UK): Links to sewage effluent cleanup and extended end-member mixing analysis. *Science of the Total Environment*, 408(6), 1315-1330

Niraula, R., Kalin, L., Srivastava, P., & Anderson, C. J. (2013). Identifying critical source areas of nonpoint source pollution with SWAT and GWLF. *Ecological Modelling, 268*(0), 123-133. doi:http://dx.doi.org/10.1016/j.ecolmodel.2013.08.007

Omernik, J.M., Abernathy, A.R. & Male, L.M. (1981). Stream nutrient levels and proximity of agricultural and forest land to streams: some relationships. *Journal of Soil& Water Conservation*, 36, 227-231.

Omernik, J.M. (1977). Non-Point Source-Stream Nutrient Level Relationships: A Nationwide Study. USEPA Ecological Research Series EPA- 600/3-77-105. USEPA. Corvallis, OR., 138pp.

Ontario Ministry of the Environment. (2006). *Water Sample Collection and Submission Protocols for Partners in the Provincial Water Quality Monitoring Network*

Ontario Ministry of Environment and Energy. (1994). *Water Management policies and guidelines, Provincial Water Quality Objectives of the Ministry of Environment and Energy. PIBS 3303E. Queen's Printer for Ontario.*

Paul, M., & Meyer, J. (2001). Streams in the urban landscape. *Annual Review of Ecology and Systematics*, *32*, 333-365.

Pratt, B., & Chang, H. (2012). Effects of land cover, topography, and built structure on seasonal water quality at multiple spatial scales. *Journal of Hazardous Materials, 209*, 48-58. doi: 10.1016/j.jhazmat.2011.12.068

Reed, B.C., Brown, J.F., VanderZee, D., Loveland, T.R., Merchand, J.W., & Ohlen, D. (1994). Measuring phenological variability from satellite imagery, *Journal of Vegetation Science,* 3:703-714

Richards, C., Johnson, L., & Host, G. (1996). Landscape-scale influences on stream habitats and biota. *Canadian Journal of Fisheries and Aquatic Sciences, 53*, 295-311. doi: 10.1139/cjfas-53-S1-295

Sanchez-Perez, J., Gerino, M., Sauvage, S., Dumas, P., Maneux, E., Julien, F., Winterton, P. & Vervier, P. (2009). Effects of wastewater treatment plant pollution on in-stream ecosystems functions in an agricultural watershed. *Annales De Limnologie-International Journal of Limnology, 45*(2), 79-92. doi: 10.1051/limn/2009011

Sardans, J. & Peñuelas, J. (2013). Tree growth changes with climate and forest type are associated with relative allocation of nutrients, especially phosphorus, to leaves and wood. *Global Ecology and Biogeography, 22*, 494–507. DOI: 10.1111/geb.12015

Schilling, K.E., & J. Spooner (2006). Effects of watershed-scale land use change on stream nitrate concentrations. *Journal of Environmental Quality, 35*:2132-2145.

Singh, A., Jakubowski, A. R., Chidister, I., & Townsend, P. A. (2013). A MODIS approach to predicting stream water quality in Wisconsin. *Remote Sensing of Environment, 128,* 74-86. doi: 10.1016/j.rse.2012.10.001

Sliva, L. & Williams, D.D.(2001). Buffer zone versus whole catchment approaches to studying land use impact on river water quality. *Water Resources*, *35*, 3462–3472.

Smith, V.H., Tilman, G.D. & Nekola, J.C. (1999). Eutrophication: impacts of excess nutrient inputs on freshwater, marine and terrestrial ecosystems, *Environmental Pollution, 100*:179-196, Retrieved from: www.elsevier.com/locate/envpol PII: S0269-7491(99)00091-3

Statistics Canada (2011). 2011 Census profile – population center, Alymer, Arthur, Belmont, Clinton, Elmira, Exeter, Ingersoll, Listowel, Lucan, Milverton, Mitchell, Mount Elgin, Seaforth, Simcoe, (London) Southland, Stratford, Strathroy, St. Thomas, Thamesford, Townsend, Waterford, Wellesley, Wilmot, Woodstock, Vanastra (2006-2011). [Data file]. Retrieved from E-STAT http://estat.statcan.ca

Tuppad, P., Santhi, C. & Srinivasan, R. (2010). Assessing BMP effectiveness: Multiprocedure analysis of observed water quality data. *Environmental Monitoring and Assessment*, 170(1-4), 315-329.

United States Geological Survey (2010). Greenness of the Conterminous Unite States. What is NDVI? Retrieved from: http://ivm.cr.usgs.gov/

Vadas, P. A., & Powell, J. M. (2013). Monitoring nutrient loss in runoff from dairy cattle lots. *Agriculture, Ecosystems & Environment, 181*(0), 127-133. doi:http://dx.doi.org/10.1016/j.agee.2013.09.025

Vannote, R.L., Minshall, G.W., Cummins, K. W., Sedell, J.R. & Cushing, C.E. (1980). The river continuum concept. *Canadian journal of fisheries and aquatic sciences, 37*(1), 130-137.

Vitousek, P. M., J. Aber, R.W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, W. H. Schlesinger, & Tilman, G. D. (1997). Human alteration of the global nitrogen cycle: Causes and consequences. *Ecological Applications,* 7:737-750

Walker, R. R. & Tossell, R. W. (1992) Environmental Monitoring of SWEEP Pilot Watersheds. Final Report, Volumess 1 and 2., Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario, Canada.

Wang, J., Jin, Peng, Bishop, P.L. & Li, Fuzhi (2012). *Upgrade of three municipal wastewater treatment lagoons using a high surface area*, *Frontiers of Environmental Science & Engineering*, 6(2), pp 288-293, DOI 10.1007/s11783-011-0280-z

Wang, L., Lyons, J., & Kanehl, P. (2002). Effects of watershed best management practices on habitat and fish in Wisconsin streams. *Journal of the American Water Resources Association, 38*(3), 663-680.

Whiles, M., Brock, B., Franzen, A., & Dinsmore, S. (2000). Stream invertebrate communities, water quality, and land-use patterns in an agricultural drainage basin of northeastern Nebraska, USA. *Environmental Management, 26*(5), 563-576. doi: 10.1007/s002670010113

Willmott CJ. (1982). Some comments on the evaluation of model performance. *Bulletin of the American Meteorological Society* **63**: 1309–1313.

Willmott CJ. (1984). On the evaluation of model performance in physical geography. In *Spatial Statistics and Models,* Gaile GL, Willmott CJ (eds). D. Reidel: Boston, 443–460.

Willmott, C.J. & Matsuura K. (2005). Advantages of the mean absolute error (MAE) over the root mean square error (RMSE) in assessing average model performance. *Climate Research* **30**: 79–82.

Willmott, C.J., Robeson, S.M., & Kenji Matsuura (2012). Short communication. A refined index of model performance. *International Journal of Climatology*. *32*: 2088–2094

Withers, P.J.A., Ulen, B., Stamm, C., Bechmann, M. (2003). Incidental phosphorus losses—are they significant and can they be predicted? *Journal of Plant Nutrients and Soil Science*, *166*:459– 68.

Withers, P.J.A., Jarvie, H.P., Hodgkinson, R.A., Palmer-Felgate, E.J., Bates, A., Neal, M., Howells, R., Withers, C.M., & Wickham, H.D. (2009). Characterization of Phosphorus Sources in Rural Watersheds. *Journal of Environmental Quality, 38*(5): 1998-2011.

Wright, J. F., Sutcliffe, D. W., & Furse, M. T. (2000). Assessing the Biological Quality of Fresh Waters: RIVPACS and Other Techniques. Freshwater Biological Assn., London. Chapter 4. *Classification of the Biological quality of rivers in England and Wales*.

Yates, A., Bailey, R., & Schwindt, J. (2006a). No-till cultivation improves stream ecosystem quality. *Journal of Soil and Water Conservation, 61*(1), 14-19.

Yates, A. G., & Bailey, R. C. (2006b). The stream and its altered valley: Integrating landscape ecology into environmental assessments of agro-ecosystems. *Environmental Monitoring and Assessment, 114*(1-3), 257-271. doi: 10.1007/s10661-006-4779-x

Yates, A. G., Bailey, R. C., & Schwindt, J. A. (2007). Effectiveness of best management practices in improving stream ecosystem quality. *Hydrobiologia, 583*, 331-344.

Yuan, Y., Lockeb, M. A., Bingnerb, R.L., Rebichc, R.A. (2013). Phosphorus losses from agricultural watersheds in the Mississippi Delta. *Journal of Environmental Management*, Volume 115, 14–20.

Zar, J.H. (1999). Bio statistical Analysis, 4th edition, Prentice Hall Inc., Upper Saddle River, N.J. p. 420-421.

Zhang, G., Guhathakurta, S., Dai, G., Wu, L., Yan, L. (2013). The Control of Land-Use Patterns for Storm water Management at Multiple Spatial Scales. *Environmental Management*, *51*(3).

10 Appendix A

Appendix A: land use descriptions and location for 29 streams and their associated catchment studied in southern Ontario.

SITE	STREAM	PWQMN STATION	Area (km²)	ONGITUI	ATITUD	Urb-C (%)	Ag-C (%)	Urb-buf (%)	Ag-buf (%)	Urb12 (%)	Ag12 (%)	Urb600 (%)	Ag600 (%)	STP-effluent (m³)	STP-persons (per km²)	STP-distance (m)
1	Ausable River	8002201602	113	-81.509	43.362	2.81	85.92	2.04	77.84	1.46	83.64	4.44	17.78	676,326	42.50	1180
2	Avon River	4001302502	116	-81.019	43.366	14.73	71.95	13.93	68.77	11.15	73.51	43.75	26.56	2,914,588	266.80	1767
3	Bayfield River	8004000802	463	-81.589	43.551	1.86	87.37	1.55	73.97	1.14	84.70	4.44	6.67	557,793	13.81	58703
6	Beauchamps Drain	8005604102	102	-81.249	43.704	0.45	86.57	1.01	85.45	1.30	88.09	0.00	77.36	0	0.00	0
12	Boyle Drain	8005602002	214	-81.092	43.693	0.87	91.89	1.05	90.67	1.18	91.36	0.00	36.00	18,220	7.11	25345
13	Canagagigue Creek	16018401602	114	-80.535	43.585	6.00	83.33	6.90	76.33	7.31	77.91	17.39	71.74	753,234	87.18	1619
14	Catfish Creek	16009700502	143	-81.043	42.776	5.15	85.99	7.86	77.39	4.67	82.70	2.27	43.18	646,048	50.72	5935
15	Conestogo River	16018407502	332	-80.670	43.757	1.86	86.87	1.87	81.48	1.54	82.85	66.67	33.33	248,002	7.30	25782
18	Dingman Creek	4001302902	133	-81.314	42.914	27.50	62.15	20.95	61.82	22.42	62.63	27.91	0.00	50,309	9.05	7173
19	Fish Creek	4001309002	145	-81.237	43.221	0.70	91.42	0.71	80.87	0.69	84.91	0.00	60.00	0	0.00	0
22	Kettle Creek	16008701002	394	-81.218	42.693	8.97	78.31	7.47	65.83	6.93	73.63	0.00	34.69	3,369,932	110.57	58360
23	Little Ausable River	8002201002	142	-81.448	43.181	2.09	91.72	3.90	81.44	4.26	84.74	3.39	5.08	139,210	14.57	6188
24	Lynn River	16015900302	137	-80.289	42.823	6.98	60.94	5.89	41.61	2.59	52.82	0.00	0.00	44,135	107.98	1552
26	Middle Maitland River	8005602602	416	-81.126	43.718	2.12	88.38	1.61	86.04	1.44	87.05	0.00	26.19	54,054	20.16	53222
28	Middle Thames River	4001304102	314	-80.998	43.031	1.32	84.61	0.91	73.86	0.61	79.15	0.00	64.44	323,118	6.34	2382
29	Moorefield Creek	16018409102	118	-80.749	43.758	1.23	85.33	1.53	76.75	1.34	79.94	12.50	57.14	0	0.00	0
30	Nanticoke Creek	16016400102	192	-80.077	42.810	2.44	72.34	2.29	57.89	1.50	68.39	0.00	42.50	29,004	20.03	61389
31	Nith River	16018403202	550	-80.679	43.375	3.00	85.43	3.60	80.43	2.37	81.81	40.28	48.61	27,825	40.34	35382
32	Nith River	16018407402	316	-80.835	43.484	1.19	90.45	0.98	89.62	0.88	89.42	6.78	91.53	0	0.00	0
33	North Thames River	4001304402	314	-81.207	43.451	2.06	91.64	2.05	89.70	1.57	90.17	4.17	47.22	519,227	14.15	780
38	Reynolds Creek	4001309102	149	-80.957	42.989	0.81	88.33	1.47	79.15	1.71	77.03	4.35	95.65	0	0.00	0
39	South Maitland River	8005603702	371	-81.541	43.685	0.97	87.92	0.66	81.85	0.68	85.75	2.99	43.28	0	0.00	0
40	South Thames River	4001304202	537	-80.927	43.019	9.55	77.51	7.76	65.20	6.70	68.69	1.61	24.19	5,361,543	22.62	94235
41	South Thames River	4001301602	270	-80.779	43.126	6.77	79.94	4.15	70.03	4.52	72.92	35.90	0.00	4,002,908	138.34	45036
42	South Thames River	4001308002	150	-80.692	43.215	2.49	87.90	1.36	81.33	1.65	82.78	19.15	21.28	200,301	18.56	28142
48	Waubuno Creek	4001309702	97	-81.117	42.995	0.81	87.43	0.80	76.58	0.43	80.84	11.11	0.00	0	0.00	0
49	Whitemans Creek	16018410602	403	-80.384	43.126	1.82	75.24	1.26	59.48	1.28	64.24	0.00	0.00	0	0.00	0
51	Catfish Creek	16009700302	349	-81.046	42.702	4.35	84.57	4.25	73.73	3.68	81.42	0.00	10.87	646,048	20.77	23190
52	Kettle Creek	16008701602	331	-81.214	42.778	6.61	81.76	5.75	71.46	5.06	79.67	36.96	4.35	163,514	5.56	24591

11 Appendix B

Appendix B: The relationship between mean catchment NDVI and water chemistry at 10 sample times (Julian day) collected between May through November 2012 for 29 streams located in southwestern Ontario. B.) Cumulative NDVI and water chemistry for sample days 161 – 321. C.) Δ NDVI and Δ stream nutrient concentration for 9 samples.

	Julian day									
Nutrient	**129**	**161**	**177**	**193**	**209**	**225**	**257**	**289**	**305**	**321**
NH_3	0.034	0.018	0.000	0.133	0.156	0.011	0.056	0.040	0.094	0.085
TKN	0.039	0.002	0.000	0.097	0.010	0.000	0.032	0.062	0.212	0.098
$NO_{3-} + NO_{2-}$	0.008	0.022	0.002	0.003	0.001	0.058	0.029	0.024	0.100	0.043
TN	0.008	0.021	0.000	0.001	0.017	0.041	0.025	0.042	0.088	0.052
SRP	0.085	0.041	0.000	0.014	0.031	0.055	0.043	0.039	0.000	0.007
TDP	0.071	0.018	0.000	0.007	0.035	0.035	0.038	0.020	0.000	0.010
TP	0.053	0.072	0.000	0.008	0.020	0.018	0.039	0.005	0.006	0.015

12 Appendix C

Appendix C: The relationship between ccumulative NDVI and water chemistry at 9 sample times (Julian day) collected between May through November 2012 for 29 streams located in southwestern Ontario.

		Julian day								
	Nutrient	**129-161**	**129-177**	**129-193**	**129-209**	**129-225**	**129-257**	**129-289**	**129-305**	**129-321**
Cumulative Frequency	**NH_3**	0.003	0.033	0.009	0.061	0.201	0.009	0.011	0.027	0.049
	TKN	0.103	0.006	0.011	0.006	0.021	0.024	0.048	0.044	0.159
	NO_{3-} + NO_{2-}	0.003	0.004	0.002	0.002	0.009	0.022	0.012	0.006	0.049
	TN	0.003	0.004	0.010	0.001	0.000	0.015	0.009	0.036	0.053
	SRP	0.062	0.048	0.010	0.000	0.009	0.002	0.029	0.041	0.033
	TDP	0.049	0.016	0.011	0.001	0.001	0.000	0.023	0.025	0.041
	TP	0.051	0.043	0.009	0.003	0.000	0.010	0.000	0.000	0.017

13 Appendix D

Appendix D: The relationship between Δ NDVI and Δ stream nutrient concentration at 9 sample times (Julian day) collected between May through November 2012 for 29 streams located in southwestern Ontario.

		Julian day								
	Nutrient	161	177	193	209	225	257	289	305	321
Delta	NH_3	0.015	0.022	0.080	0.173	0.029	0.106	0.003	0.006	0.006
	TKN	0.049	0.023	0.076	0.150	0.002	0.012	0.048	0.000	0.031
	$NO_{3-} + NO_{2-}$	0.038	0.029	0.032	0.009	0.081	0.023	0.030	0.006	0.067
	TN	0.032	0.034	0.084	0.007	0.005	0.017	0.007	0.005	0.077
	SRP	0.048	0.020	0.062	0.011	0.000	0.004	0.003	0.004	0.001
	TDP	0.053	0.021	0.062	0.007	0.051	0.003	0.000	0.004	0.001
	TP	0.090	0.025	0.075	0.002	0.021	0.001	0.002	0.021	0.001

14 Appendix E

Appendix E: Nutrient parameters for 29 streams sampled between May through November 2012. Red bolded values exceed CEQG guidelines for NH_3-N (0.019mg/L), CEQG guidelines for NO_3 (13.0mg/L), PWQO guidelines for nitrite (0.06mg/L) and PWQO guidelines for TP (0.03mg/L). Sites highlighted in grey contain ≥1 STP within the catchment. QA identified outlier data for site 38 on July 3, 2012, thus data from this date was not included in the calculation of the May through November mean of any nutrient parameter.

SITE	Sampling Date	TRIP	NH_3-N (mg/L)	NO_3+NO_2 (mg/L)	TP-P (mg/L)
1	May-15-2012	1	0.0110	4.39	**0.2720**
1	Jun-05-2012	2	0.0330	11.60	**0.1240**
1	Jul-04-2012	3	0.1680	4.18	**0.3240**
1	Jul-17-2012	4	0.0350	1.56	**0.1930**
1	Jul-31-2012	5	0.0280	1.91	**0.0825**
1	Aug-14-2012	6	0.0160	5.76	**0.2080**
1	Sep-11-2012	7	0.0220	2.75	**0.1150**
1	Oct-02-2012	8	0.0090	5.68	**0.1060**
1	Oct-23-2012	9	0.0520	1.93	**0.2970**
1	Nov-21-2012	10	0.0070	7.56	**0.0723**
2	May-16-2012	1	0.5520	5.89	**0.1050**
2	Jun-06-2012	2	0.5670	**16.50**	**0.0849**
2	Jul-06-2012	3	0.1410	8.01	**0.1230**
2	Jul-18-2012	4	1.1400	5.15	**0.1540**
2	Aug-01-2012	5	0.0250	9.04	**0.1280**
2	Aug-15-2012	6	0.0220	8.08	**0.0807**
2	Sep-12-2012	7	0.0610	11.90	**0.1020**
2	Oct-03-2012	8	0.0270	10.90	**0.1360**
2	Oct-24-2012	9	0.0760	4.37	**0.0876**
2	Nov-22-2012	10	0.1630	12.60	**0.1170**
3	May-15-2012	1	0.0080	1.50	0.0127
3	Jun-05-2012	2	0.0170	**15.40**	0.0152
3	Jul-04-2012	3	0.1300	1.41	**0.3460**
3	Jul-17-2012	4	0.0110	0.75	0.0243
3	Jul-31-2012	5	0.0160	0.53	0.0212
3	Aug-14-2012	6	0.0130	0.76	0.0212
3	Sep-11-2012	7	0.0050	0.93	0.0146
3	Oct-02-2012	8	0.0050	0.78	0.0121
3	Oct-23-2012	9	0.0160	4.07	**0.0510**

3	Nov-21-2012	10	0.0060	6.43	0.0075
6	May-15-2012	1	0.0160	2.28	0.0197
6	Jun-05-2012	2	0.0280	10.20	0.0177
6	Jul-04-2012	3	0.0090	1.94	**0.0722**
6	Jul-17-2012	4	0.0090	1.24	**0.0700**
6	Jul-31-2012	5	0.0250	1.20	**0.1270**
6	Aug-14-2012	6	0.0350	6.25	**0.0616**
6	Sep-11-2012	7	0.0190	1.71	**0.0595**
6	Oct-02-2012	8	0.0050	1.99	**0.0319**
6	Oct-23-2012	9	0.0320	7.90	**0.2190**
6	Nov-21-2012	10	0.0100	7.76	0.0146
12	May-15-2012	1	0.0140	0.60	0.0217
12	Jun-05-2012	2	0.0230	**13.40**	0.0227
12	Jul-04-2012	3	0.1720	0.44	**0.1020**
12	Jul-17-2012	4	0.0060	0.25	**0.0772**
12	Jul-31-2012	5	0.0520	0.05	**0.0718**
12	Aug-14-2012	6	0.0280	0.20	**0.0377**
12	Sep-11-2012	7	0.0160	0.36	**0.0333**
12	Oct-02-2012	8	0.0190	0.21	**0.0309**
12	Oct-23-2012	9	0.0120	5.83	**0.0606**
12	Nov-21-2012	10	0.0090	6.44	0.0284
13	May-16-2012	1	0.0170	3.46	**0.0563**
13	Jun-06-2012	2	0.0480	6.16	**0.0619**
13	Jul-06-2012	3	0.0410	2.15	**0.1040**
13	Jul-18-2012	4	0.0610	2.07	**0.1140**
13	Aug-01-2012	5	0.0840	1.92	**0.1220**
13	Aug-15-2012	6	0.0720	2.33	**0.1250**
13	Sep-12-2012	7	0.0550	1.89	**0.1220**
13	Oct-03-2012	8	0.1000	1.52	**0.1540**
13	Oct-24-2012	9	0.1740	3.58	**0.1460**
13	Nov-22-2012	10	0.2470	5.29	**0.0739**
14	May-14-2012	1	0.0150	2.97	**0.0347**
14	Jun-04-2012	2	0.0910	15.60	**0.0805**
14	Jul-03-2012	3	0.0300	0.80	**0.1650**
14	Jul-16-2012	4	0.0430	0.45	**0.1620**
14	Jul-30-2012	5	0.0470	0.65	**0.1710**
14	Aug-13-2012	6	0.0680	1.82	**0.2070**
14	Sep-10-2012	7	0.0460	6.66	**0.1760**
14	Oct-01-2012	8	0.0220	4.89	**0.0863**

14	Oct-22-2012	9	0.0490	12.40	**0.1060**
14	Nov-20-2012	10	0.1150	6.07	**0.1050**
15	May-16-2012	1	0.0130	2.18	0.0155
15	Jun-06-2012	2	0.0190	**14.70**	0.0154
15	Jul-06-2012	3	0.0510	0.07	**0.0339**
15	Jul-18-2012	4	0.0150	0.02	**0.0649**
15	Aug-01-2012	5	0.0260	0.05	**0.0344**
15	Aug-15-2012	6	0.0220	0.12	**0.0311**
15	Sep-12-2012	7	0.0130	0.09	0.0292
15	Oct-03-2012	8	0.0300	0.26	0.0298
15	Oct-24-2012	9	0.0180	8.74	**0.1180**
15	Nov-22-2012	10	0.0100	6.27	0.0081
18	May-14-2012	1	0.0970	1.89	**0.0502**
18	Jun-04-2012	2	0.1190	9.32	**0.0730**
18	Jul-03-2012	3	0.0360	2.29	**0.0570**
18	Jul-16-2012	4	0.0810	0.73	**0.0969**
18	Jul-30-2012	5	0.0760	2.06	**0.0715**
18	Aug-13-2012	6	0.0510	1.05	**0.1360**
18	Sep-10-2012	7	0.0390	0.96	**0.0820**
18	Oct-01-2012	8	0.0260	3.13	**0.0414**
18	Oct-22-2012	9	0.0230	1.07	**0.1030**
18	Nov-20-2012	**10**	0.0200	3.04	**0.0335**
19	May-15-2012	1	0.0140	1.51	0.0278
19	Jun-05-2012	2	0.0290	**19.80**	**0.0344**
19	Jul-04-2012	3	0.0550	0.34	**0.0695**
19	Jul-17-2012	4	0.0240	0.22	**0.0808**
19	Jul-31-2012	5	0.0380	0.30	**0.0631**
19	Aug-14-2012	6	0.0400	0.19	**0.0669**
19	Sep-11-2012	7	0.0170	0.16	**0.0422**
19	Oct-02-2012	8	0.0050	0.20	0.0187
19	Oct-24-2012	9	0.0050	1.51	**0.0476**
19	Nov-20-2012	10	0.0150	7.54	0.0137
22	May-14-2012	1	0.0130	4.55	**0.0967**
22	Jun-04-2012	2	0.2420	**20.40**	**0.1960**
22	Jul-03-2012	3	0.0390	8.84	**0.1990**
22	Jul-16-2012	4	0.1010	8.96	**0.3100**
22	Jul-30-2012	5	0.0130	4.73	**0.1850**
22	Aug-13-2012	6	0.0140	3.59	**0.2060**
22	Sep-10-2012	7	0.0070	3.51	**0.1580**

22	Oct-01-2012	8	0.0060	7.48	**0.1890**
22	Oct-22-2012	9	0.0070	2.46	**0.1320**
22	Nov-20-2012	10	0.0320	6.03	**0.0938**
23	May-15-2012	1	0.0270	2.28	0.0272
23	Jun-05-2012	2	0.0330	**23.30**	**0.0392**
23	Jul-04-2012	3	0.0180	1.90	**0.0553**
23	Jul-17-2012	4	0.0830	0.12	**0.0764**
23	Jul-31-2012	5	0.0410	0.06	**0.0508**
23	Aug-14-2012	6	0.0050	0.03	**0.0852**
23	Sep-11-2012	7	0.0070	0.02	**0.0779**
23	Oct-02-2012	8	0.0080	0.04	**0.0347**
23	Oct-23-2012	9	0.0210	8.52	0.0286
23	Nov-20-2012	10	0.0090	8.42	0.0120
24	May-17-2012	1	0.1270	3.12	**0.0374**
24	Jun-07-2012	2	0.0720	2.57	**0.0930**
24	Jul-09-2012	3	0.0550	4.17	**0.0767**
24	Jul-19-2012	4	0.0300	2.61	**0.0584**
24	Aug-02-2012	5	0.0260	2.76	**0.0425**
24	Aug-16-2012	6	0.1770	2.38	**0.0610**
24	Sep-13-2012	7	0.0760	3.04	**0.0561**
24	Oct-11-2012	8	0.1450	4.27	**0.0616**
24	Oct-25-2012	9	0.0820	3.75	**0.0437**
24	Nov-19-2012	10	0.0300	4.34	**0.0713**
26	May-15-2012	1	0.0120	1.40	0.0208
26	Jun-05-2012	2	0.0270	10.90	0.0225
26	Jul-04-2012	3	0.0860	0.74	**0.1260**
26	Jul-17-2012	4	0.0930	1.52	**0.1520**
26	Jul-31-2012	5	0.0440	0.15	**0.1030**
26	Aug-14-2012	6	0.0360	0.69	**0.0664**
26	Sep-11-2012	7	0.0140	0.29	**0.0662**
26	Oct-02-2012	8	0.0180	1.22	**0.0453**
26	Oct-23-2012	9	0.0210	4.74	**0.0498**
26	Nov-21-2012	10	0.0110	5.26	0.0310
28	May-17-2012	1	0.0090	3.84	0.0207
28	Jun-07-2012	2	0.0190	10.90	0.0196
28	Jul-04-2012	3	0.0370	3.29	**0.0661**
28	Jul-16-2012	4	0.0220	2.15	**0.0492**
28	Jul-30-2012	5	0.0210	2.93	**0.0549**
28	Aug-13-2012	6	0.0180	2.85	**0.0388**

28	Sep-10-2012	7	0.0050	3.65	**0.0335**
28	Oct-11-2012	8	0.0160	4.49	0.0207
28	Oct-25-2012	9	0.0120	4.00	0.0274
28	Nov-23-2012	10	0.0100	6.29	0.0149
29	May-16-2012	1	0.0100	2.63	0.0229
29	Jun-06-2012	2	0.0180	5.76	0.0169
29	Jul-06-2012	3	0.0050	0.01	**0.0715**
29	Jul-18-2012	4	0.0130	0.01	**0.0540**
29	Aug-01-2012	5	0.0050	0.01	**0.0487**
29	Aug-15-2012	6	0.0130	0.01	**0.0513**
29	Sep-12-2012	7	0.0070	0.02	**0.0303**
29	Oct-03-2012	8	0.0870	0.49	**0.1200**
29	Oct-24-2012	9	0.0140	4.74	**0.0416**
29	Nov-22-2012	10	0.0090	4.65	0.0151
30	May-17-2012	1	0.0620	0.59	**0.0379**
30	Jun-07-2012	2	0.0550	3.16	**0.1780**
30	Jul-09-2012	3	0.1800	0.21	**0.1660**
30	Jul-19-2012	4	0.1680	0.20	**0.1500**
30	Aug-02-2012	5	0.1320	0.08	**0.1370**
30	Aug-16-2012	6	0.0250	0.32	**0.1030**
30	Sep-13-2012	7	0.0250	0.31	**0.0690**
30	Oct-11-2012	8	0.0240	0.01	**0.0407**
30	Oct-25-2012	9	0.0480	3.09	**0.1920**
30	Nov-19-2012	**10**	0.0110	**2.12**	**0.0270**
31	May-16-2012	1	0.0450	0.96	**0.0358**
31	Jun-06-2012	2	0.0290	**25.70**	**0.0635**
31	Jul-06-2012	3	0.0080	0.43	**0.0692**
31	Jul-18-2012	4	0.0190	0.10	**0.0640**
31	Aug-01-2012	5	0.0100	0.07	**0.0566**
31	Aug-15-2012	6	0.0470	0.19	**0.0692**
31	Sep-12-2012	7	0.0190	0.13	**0.0426**
31	Oct-03-2012	8	0.0180	0.82	**0.0584**
31	Oct-24-2012	9	0.0410	4.32	**0.1540**
31	Nov-22-2012	10	0.0190	5.63	0.0215
32	May-16-2012	1	0.0100	0.56	0.0242
32	Jun-06-2012	2	0.0160	**27.00**	**0.0317**
32	Jul-06-2012	3	0.0180	0.05	**0.0324**
32	Jul-18-2012	4	0.0130	0.05	**0.0445**
32	Aug-01-2012	5	0.0050	0.01	0.0218

32	Aug-15-2012	6	0.0050	0.01	0.0239
32	Sep-12-2012	7	0.0050	0.02	0.0205
32	Oct-03-2012	8	0.0090	0.08	0.0188
32	Oct-24-2012	9	0.0620	10.50	0.2530
32	Nov-22-2012	10	0.0070	6.52	0.0188
33	May-15-2012	1	0.0210	7.42	**0.1090**
33	Jun-05-2012	2	0.0230	**16.20**	0.0234
33	Jul-06-2012	3	0.0850	5.07	**0.0807**
33	Jul-17-2012	4	0.0150	**25.30**	**0.2230**
33	Jul-31-2012	5	Broken	**Broken**	**0.3910**
33	Aug-14-2012	6	0.0050	1.10	**0.0572**
33	Sep-11-2012	7	0.0090	**21.10**	**0.2290**
33	Oct-02-2012	8	0.0090	0.37	**0.1220**
33	Oct-23-2012	9	0.0190	2.02	**0.0852**
33	Nov-21-2012	10	0.0120	8.46	**0.0972**
38	May-17-2012	1	0.1020	2.73	**0.0380**
38	Jun-07-2012	2	0.0500	5.43	**0.0668**
38	Jul-03-2012	3	**12.3000**	**13.20**	**3.4000**
38	Jul-16-2012	4	0.0380	4.24	**0.0581**
38	Aug-02-2012	5	0.0280	4.38	**0.0415**
38	Aug-13-2012	6	0.0540	3.64	**0.0814**
38	Sep-13-2012	7	0.0580	4.12	**0.0540**
38	Oct-11-2012	8	0.0400	3.82	**0.0401**
38	Oct-25-2012	9	0.0670	4.01	**0.0457**
38	Nov-23-2012	10	0.4580	6.09	**0.6070**
39	May-15-2012	1	0.0110	2.32	0.0113
39	Jun-05-2012	2	0.0250	12.60	0.0105
39	Jul-04-2012	3	0.0240	1.12	0.0203
39	Jul-17-2012	4	0.0250	0.42	**0.0322**
39	Jul-31-2012	5	0.0080	0.29	0.0227
39	Aug-14-2012	6	0.0100	0.30	0.0249
39	Sep-11-2012	7	0.0090	0.52	0.0162
39	Oct-02-2012	8	0.007	0.7	0.0134
39	Oct-23-2012	9	0.008	4.1	no data
39	Nov-21-2012	10	0.0070	6.90	0.0064
40	May-17-2012	1	0.0370	5.63	**0.0386**
40	Jun-07-2012	2	0.1840	5.04	**0.2700**
40	Jul-03-2012	3	0.0290	3.92	**0.0686**
40	Jul-16-2012	4	0.0250	3.89	**0.0912**

40	Aug-02-2012	5	0.0080	3.56	**0.1310**
40	Aug-13-2012	6	0.0060	2.97	**0.1200**
40	Sep-13-2012	7	0.0160	4.38	**0.0982**
40	Oct-11-2012	8	0.0150	4.81	**0.0898**
40	Oct-25-2012	9	0.0630	3.68	**0.0855**
40	Nov-23-2012	10	0.1300	6.30	**0.0535**
41	May-16-2012	1	0.1620	11.30	**0.1050**
41	Jun-07-2012	2	0.1980	9.48	**0.1770**
41	Jul-06-2012	3	0.1630	6.68	**0.1090**
41	Jul-18-2012	4	0.3610	5.96	**0.1680**
41	Aug-01-2012	5	0.0140	0.01	**0.2180**
41	Aug-15-2012	6	0.0930	3.44	**0.1940**
41	Sep-13-2012	7	0.0610	4.92	**0.1630**
41	Oct-03-2012	8	0.3110	7.26	**0.1990**
41	Oct-25-2012	9	0.2270	5.03	**0.1570**
41	Nov-19-2012	10	0.5380	7.56	**0.0867**
42	May-16-2012	1	0.0900	0.17	0.0228
42	Jun-07-2012	2	0.0220	**21.00**	**0.0644**
42	Jul-06-2012	3	0.0050	0.06	**0.1190**
42	Jul-18-2012	4	0.0200	0.04	**0.1110**
42	Aug-01-2012	5	0.0050	5.22	**0.0597**
42	Aug-15-2012	6	0.0070	0.01	**0.0510**
42	Sep-13-2012	7	0.0060	0.01	**0.0522**
42	Oct-03-2012	8	0.0100	0.01	**0.0404**
42	Oct-24-2012	9	0.0060	1.78	**0.0580**
42	Nov-19-2012	10	0.0090	6.09	0.0228
48	May-17-2012	1	0.0090	3.18	0.0158
48	Jun-04-2012	2	0.0230	**14.80**	0.0292
48	Jul-06-2012	3	0.0330	2.08	0.0296
48	Jul-16-2012	4	0.0150	1.61	**0.0307**
48	Jul-30-2012	5	0.0140	2.07	0.0294
48	Aug-13-2012	6	0.0170	2.05	**0.0328**
48	Sep-10-2012	7	0.0070	1.54	0.0263
48	Oct-01-2012	8	0.0050	2.18	0.0129
48	Oct-22-2012	9	0.0170	1.54	0.0130
48	Nov-20-2012	10	0.0150	5.52	0.0089
49	May-17-2012	1	0.0890	3.51	0.0153
49	Jun-07-2012	2	0.0160	8.72	**0.0450**
49	Jul-09-2012	3	0.0200	4.20	0.0199

49	Jul-19-2012	4	0.0170	4.46	0.0122
49	Aug-02-2012	5	0.0050	4.10	0.0120
49	Aug-16-2012	6	0.0140	3.71	0.0144
49	Sep-13-2012	7	0.0050	4.30	0.0081
49	Oct-11-2012	8	0.0080	4.15	0.0073
49	Oct-25-2012	9	0.0070	2.69	0.0145
49	Nov-19-2012	10	0.0100	4.54	0.0126
51	May-14-2012	1	0.0220	1.72	**0.0304**
51	Jun-04-2012	2	0.0980	**18.90**	**0.0895**
51	Jul-03-2012	3	0.0170	0.46	**0.0538**
51	Jul-16-2012	4	0.0140	0.23	**0.0582**
51	Jul-30-2012	5	0.0100	0.34	**0.0461**
51	Aug-13-2012	6	0.0550	1.13	**0.1070**
51	Sep-10-2012	7	0.0370	3.82	**0.1130**
51	Oct-01-2012	8	0.0050	3.29	**0.0376**
51	Oct-22-2012	9	0.0210	9.24	**0.0982**
51	Nov-20-2012	10	0.0150	4.81	**0.0389**
52	May-14-2012	1	0.0220	0.48	**0.0492**
52	Jun-04-2012	2	0.2630	**22.50**	**0.1310**
52	Jul-03-2012	3	0.0910	1.48	**0.1180**
52	Jul-16-2012	4	0.0500	4.76	**0.3350**
52	Jul-30-2012	5	0.0370	1.90	**0.1040**
52	Aug-13-2012	6	0.0210	1.19	**0.1880**
52	Sep-10-2012	7	0.0140	0.93	**0.0850**
52	Oct-01-2012	8	0.0220	1.37	**0.0689**
52	Oct-22-2012	9	0.0250	1.50	**0.0973**
52	Nov-20-2012	10	0.0360	4.67	**0.0663**

Curriculum Vitae
Renee Lazor

EDUCATION

Master's of Science, Geography – University of Western Ontario **2012 - Present**
Bachelor of Science, Geography - University of Calgary **2011**

AWARDS AND SCHOLARSHIP

Jason Lang Scholarship.
Sustainability Grant provided through the Office of Sustainability, University of Calgary.
Alexander Rutherford Scholarship.
Academic Achievement Scholarship, Crown Flex Pack.

ADDITIONAL TRAINING

CABIN Project Manager certification **2014**
Environment Canada Battle Creek River Assessment Workshop **2011**
Certified CPR and Standard First Aid (C) **2013**
WHMIS Certification **2012**
Stream Keepers Certificate of Achievement **2003**
Pacific Stream Keeper Federation in Cooperation with Canadian Fisheries and Oceans
Valid Class 5 Operator's License

WORK HISTORY

Research Assistant, University of Western Ontario May 2012 – Present

- Deploy water chemistry equipment, collect chemical and biological samples, complete cross sectional measurement of rivers for stream metabolism and nutrient concentrations
- Communicate with land owners and disseminate information to project organizers and the pubic

Junior Physical Scientist, Environment Canada October 2011 - December 2011

- Assimilated and reviewed data to complete interim and annual apportionment reports for presentation to the Prairie Provinces Water Board and Trans boundary Water Unit
- Deconstructed natural flow computations for new software and created a procedural manual for the Natural Flow Computation Program

Hydrometric Data Analyst, Environment Canada January 2011 - August 2011

- Assimilated and reviewed data to complete interim and annual apportionment reports for presentation to the Prairie Provinces Water Board and Trans boundary Water Unit

Parks Technician, Rocky View County May 2010 – September 2010

- Performed field inspections recording the status of Municipal Lands and Environmental Reserves

Independent Project, University of Calgary Office of Sustainability Jan. – May 2010

- Completed a flora and fauna survey to produce a land use management document contributing to the long term ecological function of the university grounds

GIS Research Technician, the Canadian Heritage Foundation Sept. – Dec. 2009

- Completed a statistical analysis of demographic, socio-economic and socio-cultural data for minority groups in Canada

THESIS TOPIC AND COMPETENCIES

MSc. Thesis Topic

- Identifying land use drivers of tributary nutrient concentrations and describing the magnitude and direction of their relationship are critical activities to improvement management of water quality in basins draining into the Great Lakes.
- Quantify the cumulative influence of spatial patterns in land use and land cover on variation of nutrient concentrations in tributaries of the Great Lakes.

GRANT PAPERS AND CO-OPERATIVE WORK TERM PROJECTS

Lazor, R., (2014). Land use interactions drive southern Ontario stream nutrient concentrations, Supervised by Adam Yates, Completed for fulfillment of requirements for MSc. Geography, UWO

Lazor, R., (2011). *Procedural Manual for River Basin Assessment Tool,* Supervised by Vir Khanna, Completed for Environment Canada, Prairie Provinces Water Board

Lazor, R., (2010). *Procedural Manual for Municipal Reserve Inspection and Cemetery GIS Project,* Supervised by Jeff Quigley and Greg Van Soest, Completed for the Municipal Lands Department at Rocky View County, Alberta

Lazor, R., (2010). *Understanding the Effects of Land Use Change on Local and Regional Ecosystems and Identifying Landscape Management Practices which Maintain Ecological Function,* Supervised by Joanne Perdue, Completed for the University of Calgary Office of Sustainability

Lazor, R., (2009). *Understanding Regression and Hot Spot Analysis in ArcGIS – A Study of Official Minority Language Communities in the Region of Montreal,* Supervised by Martin Durand, Completed for the Department of Canadian Heritage